ERRATA

Page 20, line 10 from top, for dependent read independent.

Page 43, Fig. 6, point K_2 should be located at intersection of K_1 K_2 and M_2 K_2.

Page 48, line 8 from bottom, for ionized read unionized.

Page 50, line 13 from top, for T read $1 \div T$, line 15 from bottom, for Jelle read Jette.

Page 58, line 3 from top, for evaporated read cooled.

Page 60, line 11 from top, for evaporated read cooled.

Page 64, lines 3 and 5 from top, for $ZnCl_2.5/2H_2O$ read $ZnCl_2.3H_2O$.

Page 65, line 2 from top, for left read right, also point F of Fig. 13 should show a more definite intersection of the two curves.

Page 66, line 3 from bottom, read also for not.

Page 71, lines 4 to 6 should read then $16.4 \div (100 - x) = 27.39 \div 100$ and $x = 40.13$. If y represents the KCl which separates, then $41 - y \div 16.4 = 35.16 \div 27.39$ and $y = 19.94$.

Page 113, line 5 from top, for $Na0H.H_20$ read $Na_20.Cr0_3$, lines 8 and 10 from top for CFE read GFE, line 6 from bottom for T read J.

Page 125, line 14 from top, for Fig. 45 read Fig. 46.

Page 128, lines 9 and 11 from bottom, interchange I and II.

Page 130, line 16 from top, for U read V.

Page 138, for lines 7 and 8 from top substitute the following: $100\,Na_2S0_4.10H_20 + 160.66\,KCl = 47.29\,K_3Na(S0_4)_2 + 49.06$ NaCl+solution of composition given above.

Page 145, line 20 from top, for AC and BC read AG and BG.

Page 158, line 14 from top, for ternary read quarternary.

Page 163, line 11 from bottom, for crystalline read crystallization.

Page 172, line 9 from bottom, for invariant read univariant.

Page 182, line 10 from top, for 1.724 read $0.963 \div 0.577$ or 1.668.

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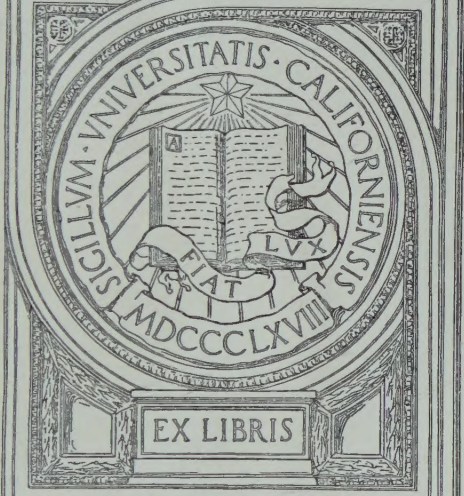

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EQUILIBRIA IN SATURATED SALT SOLUTIONS

A Summary of the Results of the Study of the Heterogeneous Equilibria Which Exist in Aqueous Solutions of Electrolytes

BY

WALTER CHARLES BLASDALE

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF CALIFORNIA

American Chemical Society
Monograph Series

BOOK DEPARTMENT

The CHEMICAL CATALOG COMPANY, *Inc.*

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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

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The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coördinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of coöperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

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PREFACE

This volume has been prepared at the suggestion of the Board of Editors of the Series of Monographs, whose publication has been undertaken by the American Chemical Society. The widespread interest in both practical and theoretical chemistry, which was one of the results of the Great War, has given rise to a demand for brief treatises dealing with a number of the special fields of chemical science. Of these the nature of the heterogenous equilibria which exist in systems composed of water and one or more electrolytes is of major importance. Although many of the technical processes in general use employ separations which involve such equilibria the available information relating to such processes is often purely empirical and fragmentary, whereas an adequate understanding of the possibilities of such processes under varying conditions clearly calls for a general and comprehensive treatment. It is one of the chief objects of this volume to show how a general treatment can be applied to the class of systems under consideration, the method employed being to discuss in turn a series of typical illustrations of such processes for which fairly complete data are available. Aside from its technical application this subject is of interest from a purely theoretical point of view and furnishes one of the many striking illustrations of the results obtained by the application of thermodynamics to the study of chemical processes. Although the subject has been approached from the point of view of thermodynamics and the modern conception of the nature of chemical forces, only those features of these theories which are essential have been made use of.

The number of systems, many of which are complex, with which the volume deals is large and the available data relating to them, although still very inadequate, are voluminous and difficult to summarize. Hence no attempt has been made to either outline or give references to articles other than those containing data actually used. This deficiency will however be supplied by one of the forthcoming volumes of the International Critical

Tables in which an attempt has been made to bring together in a condensed form all the numerical data relating to systems derived from water and one or more electrolytes. No new ideas should be looked for in this volume. The fundamental features of the subject were discovered, for the most part, many years ago, as a result of the investigations of van't Hoff, Roozeboom, Schreinemakers, Meyerhoffer, Jänecke and others. The attempt has been made to give the credit due these and other investigators at the proper places but it is possible that some omissions have been made. It is obvious that the method of presentation made use of has been influenced, either consciously or unconsciously, by the treatises already published which deal with the subject. These include especially Roozeboom's "Die heterogenen Gleichgewichte von Stanpunkte der Phasenregel" (Vieweg and Sohn, Braunschweig), Jänecke's "Gesätigte Salzlosungen" (Knappe, Halle), Clibbin's "Principles of the Phase Theory" (Macmillan and Co., London) and Findlay's "Phase Rule" (Longmans, Green and Co., London).

WALTER C. BLASDALE.

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EQUILIBRIA IN SATURATED SALT SOLUTIONS

Chapter I.

Water—A Typical One-Component System.

Peculiarities of Water. The properties which characterize liquid water are unique. It is remarkable for its great and varied solvent power and for its "polar" [1] character. The peculiarities included under the latter designation include a very high dielectric constant, extraordinary ability to cause substances dissolved in it to ionize, a moderate degree of ionization of its own molecules and a well-defined tendency for the aggregation of its molecules into complexes. This last named peculiarity involves an energy change and therefore is associated with abnormally large values for certain of its physical constants, such as specific heat, latent heat of evaporation and viscosity. Its polar properties, like those of polar substances in general, are best interpreted as the result of an unequal distribution of the plus and minus charges of which the molecule is made up and consequent electrostatic attraction of its molecules for each other when in certain relative positions. These properties find a satisfactory explanation in the theory of atomic and molecular structure which has been developed by Lewis.[2] According to this theory, owing to the ease with which the two hydrogen atoms lose and the oxygen atom takes up electrons, the two pairs of electrons which constitute the actual bond uniting these atoms are nearer to the oxygen than to the hydrogen atoms. This leaves the central oxygen atom negatively charged as compared with the two hydrogen atoms and accounts for the tendency of the molecules to form chains of loosely bound molecules.

[1] For further discussion of this term see Bray and Branch, *J. Am. Chem. Soc., 35,* 1440 (1913); also Lewis, *ibid., 35,* 1448 (1913).

[2] Lewis, *J. Am. Chem. Soc., 38,* 762 (1916); also "Valence and the Structure of Atoms and Molecules," Chemical Cat. Co., 1923.

Figure 1, in which the valence electrons are represented by dots, suggests how these relations can be expressed graphically.

Water Considered as a Pure Substance. Although the density of water vapor between 0° and 200° differs but slightly [3] from the value required by the assumption that its molecular weight corresponds to the formula H_2O, the physical properties of liquid water suggest that it is an aggregated liquid. Röntgen [4] concluded that it consisted of a mixture of $(H_2O)_3$, trihydrol, and $(H_2O)_2$, dihydrol. These suggestions, as noted by Vernon,[5] also explain the very high values for the boiling point of water as compared with the boiling points of closely related compounds, especially hydrogen sulfide, selenium sulfide, hydrogen chloride and ammonia, and the abnormally low values found by Lespieau [6] and

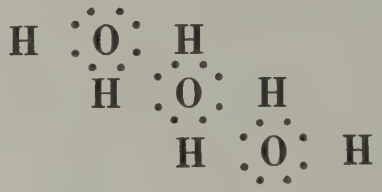

FIG. 1.—Possible structure of aggregated water molecules.

by Walker [7] for the depression of the freezing point of certain solvents by water. From a study of the results obtained by a number of investigators Sutherland [8] was able to estimate probable values for the density, surface tension, critical temperature, specific heat, viscosity and latent heat of evaporation of di- and tri-hydrol and to estimate that at 0° liquid water consisted of 37.5 per cent of trihydrol and 62.5 per cent of dihydrol. Further, since some of the molecules of liquid water are known to be dissociated into hydrogen and hydroxyl ions, liquid water must be thought of as a mixture of several molecular species. As these ions must be present in equal concentrations and since aggregation does not change the relative proportions of oxygen and hydrogen liquid water can still be represented by the formula $(H_2O)n$. A similar line of reasoning leads to the conclusion that water vapor

[3] Bose, *Z. Elektrochem., 14,* 269 (1908); Oddo, *Gazz. Chim. Ital., 45,* 319 and 395 (1915).
[4] Röntgen, *Wied. Ann., 45,* 91 (1891).
[5] Vernon, *Phil. Mag.,* (5) *31,* 387 (1891).
[6] Lespieau, *Compt. Rendu., 140,* 855 (1905).
[7] Walker, *Z. physik. Chem., 5,* 196 (1890).
[8] Sutherland, *Phil. Mag.,* (5) 197 (1890).

and all of the solid forms of water can be similarly represented.

It has been shown that a definite equilibrium, which is established almost instantly, exists between the molecules of water and the ions into which they dissociate. It is very probable that the same is true of the reaction between the simple and aggregated molecules. Since these equilibria, as well as the properties of the molecular species concerned in these equilibria, vary continuously with varying pressure and temperature the properties of water should change continuously when the external conditions to which it is subjected are changed. Experience shows that so long as one deals with water in the same state, even though this state represents a mixture of different molecular species, there is no discontinuity in any of its properties. If, however, the variations made are sufficiently large, discontinuities, which are always associated with transformations from one state to another, occur. Expressed differently, each of the forms of water is capable of existing within a certain range of conditions only, and the different forms or phases can be defined in terms of the limiting values of these conditions. The peculiarity which distinguishes pure from impure water is that these changes can be made while the conditions remain constant. For example, liquid water can be changed to water vapor by the addition of heat if the temperature is 100° C. and the pressure 760 mm.; furthermore, the process can be reversed by the abstraction of heat, and both operations can be continued indefinitely under the conditions named. The temperature and pressure can be kept constant although the ratio between the amounts of the original liquid and the distillate changes. This is not true of water associated with any substance which is appreciably soluble in it. Substances which conform to this peculiarity were designated "hylotropic" by Ostwald.[9] It constituted a convenient test for the purity of a substance.

Changes in the Properties of Water and Its States. Experience has shown that the only conditions which need be specified for the purpose of defining the properties of any one of the forms of water are pressure and temperature. If these are fixed all of those properties which are of an intensive character, such as density, viscosity, index of refraction and specific heat, are fixed; fixing the external conditions however does not fix the

[9] Ostwald, *J. Chem. Soc., 85,* 506 (1904).

mass or any of those properties which are directly proportional to mass. Since the properties of the former group are mutually interdependent it is possible to define them in terms of any two which it is found desirable to select. Just as a chosen set of values for pressure and temperature fixes the index of refraction and the density so do chosen values for the last named properties fix the pressure and temperature. Since the temperature attained and the pressure exerted by any mass of matter are the only properties which can be varied directly they are more frequently used in defining the properties of such masses than any of the others.

Properties as Variables. The intensive properties of any mass of matter may be regarded as mathematical variables but if the mass is a pure substance and if it exists in some one state only, the nature of that state and the numerical values of all these variables are fixed, provided two of them are specified. Each of the remaining intensive properties can be expressed by numerical values which are dependent upon the numerical values chosen, or, expressed differently, the system possesses one dependent variable only. The conventional device for representing such a system, where pressure and temperature and a third property, which will be represented by A are the variables, is $f(P,T,A) = 0$. This is a simple method of stating that the relations existing between the pressure, temperature and some third intensive property of a mass of a pure substance are conditioned by an equation, the form of which is not stated and is not necessarily known, in which they are the only unknown quantities. If any two of these variables have known values the third can be calculated provided the form of the function is known. Any three variables representing intensive properties may be substituted for those given in this expression.

The same convention can be used to express the relation between the variables, and therefore the properties, of the same pure substance in its other forms but the form of the function, that is the mathematical operations which it demands or the constants used in these operations, must differ from those concerned in the expression for the form first considered. In the case of water there must be as many equations of state as there are forms of water.

Simultaneous Occurrence of Two or More States. If two forms of water are in equilibrium they must be in actual contact and therefore it must be assumed that they possess the same tem-

perature and pressure. Further, the laws of thermodynamics demand that the amount of mechanical resistance which can be overcome when one mole of one form changes into the other form exactly equals that which can be overcome when the reverse takes place. Another method of representing the same requirement is to state that the free energies of equal masses of the two forms are the same. Equivalency of the two free energies demands that a certain factor, which is a measure of the intensity with which the molecules of water tend to escape from one form to the other, a property to which the name fugacity [10] has been given, be expressed by a numerical value identical with that representing the same factor for the reverse process. This factor has the properties of a pressure but should be thought of as the property which gives rise to a pressure rather than the pressure itself. The fugacities of ideal gases may be measured by determining their pressures but for gases which do not obey the gas laws quantitatively the pressure actually measured must be corrected by a quantity representing the magnitude of the deviation from the behavior of ideal gases. The fugacities of liquids and solids must be measured by indirect methods.

The fugacity of water, like its other intensive properties, is dependent upon the pressure and temperature and it is only when a fortuitous choice of these magnitudes is made that the fugacities of two different forms of water is the same and true equilibrium between them possible. Such a situation demands that the values for the pressure and temperature be such as to satisfy two equations of state which may be expressed by

$$f(\mathrm{P,T,Fu}\,\mathrm{H_2O}\ \text{vapor}) = 0$$
$$f'(\mathrm{P',T'F'u}\,\mathrm{H_2O}\ \text{liquid}) = 0$$

in which Fu and F'u represent the fugacities of water in its two forms. Since the two forms are in actual contact P must equal P' and T must equal T' and since a condition of equilibrium exists between the two forms Fu must equal F'u. The values of the three variables are limited by the conditions expressed in the two equations and therefore only one can be chosen arbitrarily. That is, if P or T or Fu is fixed the other two must be assigned those values which the two equations demand. Expressed

[10] Lewis, *Proc. Amer. Acad. Sci., 37,* 49 (1901).

more concisely, such a system can possess only one dependent variable or one "degree of freedom."

If three masses of water each representing a different form are in equilibrium there are three equations which must be complied with, but in this case also only three variables are concerned and hence it should not be possible to fix arbitrarily the values of any of these variables. That is, only one set of three variables can be found which comply with the requirements demanded by three equations. Such a system possesses no degrees of freedom or there are no dependent variables.

It should not be possible for any four of the different forms of water to exist in equilibrium. Such a system would consist of three variables limited by the conditions imposed by four equations, which is mathematically impossible.

Experimental Data Relating to Water. The effect of varying pressure and temperature upon the forms of water has been determined experimentally. The results obtained can be expressed graphically by plotting the changes in the values of these variables on two rectangular axes, as has been done in Figure 2. The curve OA [11] represents the series of pressures and temperatures at which liquid water and water vapor are in equilibrium; it is the vapor pressure curve for liquid water, and the point P is the boiling point, that is the temperature at which the vapor pressure is 760 mm. The curve OB represents the series of pressures and temperatures at which solid water (ordinary ice) and water vapor are in equilibrium; [12] it is the vapor pressure curve for ice. The curve OC represents the series of pressures and temperatures at which liquid water and ice are in equilibrium. The point O is common to all three curves and represents the pressure due to water vapor, namely, 4.6 mm., and the temperature, namely, 0°, at which all three forms are in equilibrium when the entire system is under atmospheric conditions. All of these facts are in accord with the theory outlined in the preceding paragraphs.

The figure shows only the lower portion of the curve OA, but since the difference between the densities of the liquid and vapor phases diminishes with increasing pressure and temperature this curve should end in a definite point, namely, the point at which

[11] For summary of measurements between —16° and 370° see Mellor, "Inorganic and Theoretical Chemistry," Vol. I, 432 (1922).

[12] Data from Scheel and Heuse, *Ann. Physik.*, (4) *29*, 723 (1909) and *31*, 715 (1910).

the densities of the two forms become identical. Experience confirms this assumption and it is possible, by choosing a proper sequence of temperatures and pressures, to transform liquid water into water vapor or the reverse without at any time causing a discontinuity to appear in any of its properties. The values ob-

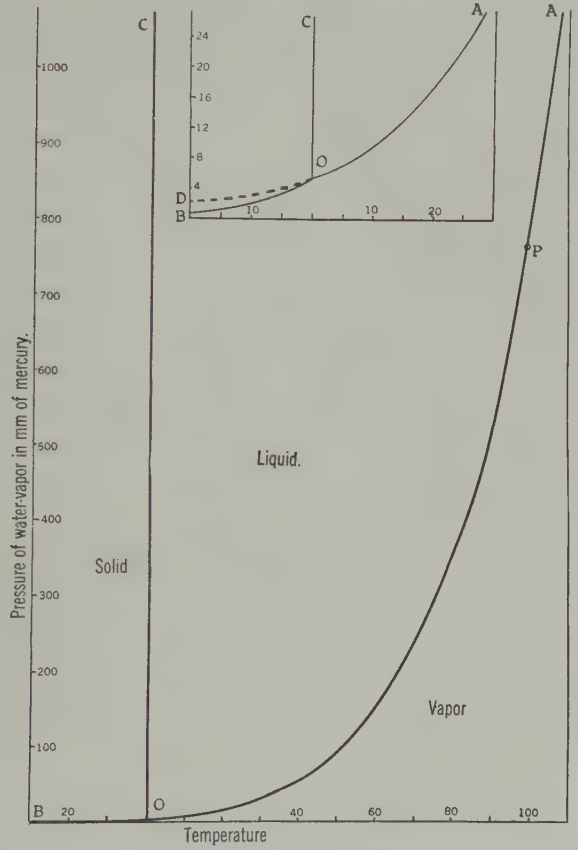

FIG. 2.—Pressure-temperature diagram for water between — 30° and 110°.

tained by Holburn and Baumann [13] for the so-called critical point are 370° and 217.5 atmospheres. The curve OB probably ends at the absolute zero, at which point water can be said to possess neither pressure nor temperature. It is possible, however, that one or more additional forms of solid water may appear

[13] Holburn and Baumann, *Ann. d. Phys.*, (4) *31*, 945 (1910).

before this temperature is reached. If so there is another triple point at which water vapor and the two solid forms are in equilibrium.

Metastable Equilibria. The curves which have been described represent "stable equilibria" because the systems represented by points on these lines will persist without change for indefinite periods of time if the conditions represented are not changed. It is possible, however, to pass down the curve AO beyond O, at least as far as the point corresponding to a temperature of — 20°. The dotted line shown on the smaller diagram at the upper part of Figure 2, which represents the lower portion of the larger diagram drawn to a larger scale, represents these facts. The pressure and temperature measurements obtained show that this portion of the curve is continuous with OA. If, however, a minute particle of ice is used to "inoculate" the system or if it is submitted to a slight mechanical shock liquid water entirely disappears, the pressure falls and the resulting equilibrium is now represented by some point on OB. Equilibria on the extended portion of the AO curve are designated by the term "metastable." Similar metastable systems corresponding to prolongations of the curve OB are to be expected but it is questionable whether they have ever been realized experimentally.

Factors Which Determine Vapor Pressure Curves. It will be noted that for points on the curves OA and OB an increase in temperature is offset by an increase in pressure. These relations can be predicted from the Theorem of Le Chatelier which states that any change in one of the external conditions tends to cause the system to react in such a manner as to diminish or to entirely eliminate the effect of the original change. If the pressure upon a system represented by a point on the line OA or OB is increased the system will respond by reacting in such a manner as to decrease its volume and therefore diminish the pressure increase, which can only be effected by the conversion of vapor into liquid or solid. In order to prevent the disappearance of the vapor phase when the pressure is increased it is necessary to increase the temperature also. If the temperature of such a system is increased it will react in such a manner as to absorb heat, which can only be effected by the conversion of liquid or solid into vapor.

The Clausius-Clapeyron Equation. A quantitative formulation of the Theorem of Le Chatelier is found in the Clausius-Clapeyron equation. In a preceding paragraph it has been stated that equilibria represented by points on any of the three curves necessitate identical values for the fugacities of the two forms which are in equilibrium. It can be shown to be a consequence of the two laws of thermodynamics that the rate at which the fugacity changes with the pressure, if the temperature is kept constant, is proportional to the volume occupied by a unit mass of the phase concerned. Since the volume of a unit mass of water vapor greatly exceeds that of a unit mass of liquid, increasing the pressure must increase the fugacity of the vapor more rapidly than that of the liquid. Further, the difference in the volumes of the two forms will determine the extent to which the increase in the fugacity of one form exceeds the increase in the fugacity of the other when the pressure under which two forms in equilibrium is increased. Similarly it can be shown that the rate at which the fugacity increases with increasing temperature, if the pressure is kept constant, is proportional to the heat content of a unit mass of the phase concerned. Since the heat content of water vapor exceeds that of liquid water, increasing the temperature must increase the fugacity of the vapor more rapidly than of the liquid. Further, the difference in the heat capacity of the two forms will determine the extent to which the increase in the fugacity of one form exceeds the increase in the fugacity of the other when the temperature at which the two forms are in equilibrium is increased. In order to maintain identical values for the fugacities of the two forms both temperature and pressure must be increased, but not at the same rate. The quantitative expression for this condition is given in the form of the Clausius-Clapeyron equation which is

$$\frac{dp}{dT} = \frac{\Delta H}{T(V_2 - V_1)}$$

In this expression $\frac{dp}{dT}$ represents the rate at which the pressure must be increased as compared with the rate at which the temperature must be increased in order to keep the fugacities of the two phases constant. ΔH represents the latent heat of vaporization of one gram mole of water if the equilibria concern liquid and vapor phases, the latent heat of sublimation if they concern

the solid and vapor phases. These values vary somewhat with the temperature, and although the equation is frequently used in calculating vapor pressures, etc., for wide ranges of temperatures it is not strictly true unless the value of ΔH for the particular temperature concerned is known. $V_2 - V_1$ represents the volume change associated with the process for which ΔH measures the heat change, and it also changes with the temperature concerned. The expression $\frac{dp}{dT}$ represents the slope of the curves OA, OB and OC at any chosen point on these curves. Since the values of ΔH for points on OA and OB decrease but slowly with increasing temperature as compared with values of $V_2 - V_1$, the slope of these curves is very largely determined by the latter values. If the vapor present is assumed to be a perfect gas and if the volume occupied by one mole of the liquid be neglected, the form of the Clapeyron equation can be changed by substituting $RT \div p$ for $(V_2 - V_1)$, which yields the well-known equation of van't Hoff, namely,

$$\frac{d \ln p}{dT} = \frac{\Delta H}{RT^2}$$

Although this equation is only approximate, since water vapor is not a perfect gas, it is possible to calculate from it with a fair degree of accuracy the actual values of points on the three curves provided the values for two points are known. The equation can be used with a greater degree of accuracy if fugacities are substituted for pressures.

The Water Diagram for Ideal Conditions. The data represented by the curves OA and OB of Figure 2 were obtained by making pressure-temperature measurements in open vessels. If similar experiments were made in closed vessels from which the air had been removed it would be found that the total pressure within the vessels would agree almost exactly with the partial pressures due to water vapor when under atmospheric conditions. The presence of the nitrogen, oxygen, argon, etc., of the atmosphere affects the properties of solid and liquid water only in proportion to the extent to which they are dissolved. Although these gases are appreciably soluble in water the actual molal concentrations in saturated water, even at zero degrees, and at pressures

corresponding to normal atmospheric conditions, are extremely small and for most purposes the properties of such solutions can be considered to be identical with those of pure water. The effect of increasing total pressure upon the vapor pressure of water can be shown to depend upon the ratio between the volume occupied by unit weight of the liquid or solid and the volume occupied by an equal weight of the vapor when at a pressure corresponding to the vapor pressure. Since this ratio, at least for moderate ranges of temperature, is very small this effect can also be disregarded unless extreme accuracy is demanded. The net effect of assuming ideal rather than atmospheric conditions is to shift by negligible amounts the curves OA and OB below the positions indicated in the figure.

The Freezing Point Curve. If the pressure on systems corresponding to points on the curves OA and OB is increased, even by an infinitesimal amount, by reducing the volume of the containing vessel, and if all air and other gases have been excluded, the vapor must entirely disappear if the temperature is kept constant. Increasing the pressure upon the system liquid water-solid water under similar conditions must also cause the disappearance of one phase, but this effect can be prevented by a very slight change in temperature. Since the volume occupied by solid water slightly exceeds that occupied by the same amount of liquid, increasing the pressure should change solid to liquid, but this might be prevented by a decrease in temperature. The rate at which the temperature must be decreased to offset an increase of one atmosphere has been calculated by the Clapeyron equation to be .0075°, a result which agrees with the experimental determinations. If it is desired to complete the diagram for the system water, by assuming pressures greater than those due to the vapor of water only, it is necessary to add the curve OC which represents the effect of pressure upon the temperature necessary for maintenance of an equilibrium between liquid water and ice. Owing to the very small volume change as compared with the heat change, with which this transformation is associated the curve slopes from the triple point towards the vertical axis but slightly; actual experiment has shown that a pressure of 590 atmospheres was required to reduce the temperature from 0° to − 5°. This equilibrium is correctly represented by OC.

The work of Tammann [14] and of Bridgeman [15] has shown that this curve actually ends at a second triple point corresponding to $-22°$ and 2047 atmospheres, at which point a second solid modification appears. By measuring the volume changes associated with pressure and temperature changes these experimenters obtained evidence for the existence of four different solid modifications of water in addition to ice. They fixed the range of pressures and temperatures within which these modifications were stable and located five additional triple points on the pressure-temperature diagram. Their results are represented in Figure 3,

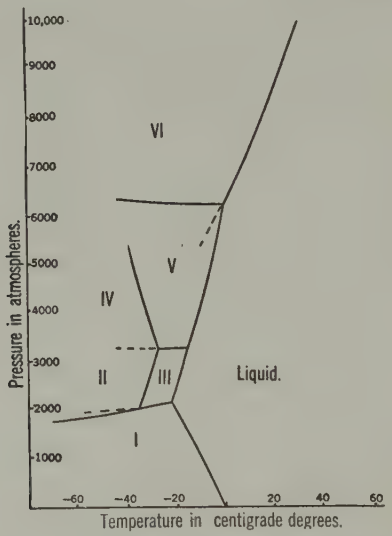

FIG. 3.—The system water at high pressures and low temperatures.

in which Roman numerals are used to represent the various solid phases.

It has been stated that equilibrium represented by the point O of Figure 2 can exist only when $T = 273°$ and $p = 4.6$ mm. This statement involved the assumption that water was the only component present. If air or any other substance which is capable of dissolving in any one of the various forms of water at its triple point is also present, it is possible for the system to exist over a limited range of pressure and temperature conditions,

[14] Tammann, *Z. physik. Chem.*, *72*, 609 (1910).
[15] Bridgeman, *Z. anorg. Chem.*, *77*, 377 (1912).

owing to the fact that an additional component is present and therefore an additional mathematical variable is concerned in the system. The completed diagram as here shown involves an inconsistency unless it is understood that the pressure axis represents two different quantities according to whether the curves OA and OB, on the one hand, or the curve OC, on the other, are under consideration. For the curves OA and OB the pressure indicated is that due to water vapor only, or, if the total pressure amounts to a few atmospheres only, it represents with sufficient accuracy the partial pressure of the water vapor in the vapor phase; for the curve OC it represents the total pressure of the system in which there is no vapor present, hence the pressure concerned must be that exerted by the walls of the containing vessel.

Chapter II.

Systems Derived from Water and a Single Salt Which does not Form Hydrates.

Peculiarities of Salts. With the exception of mercuric chloride, cadmium iodide, and a limited number of haloid salts, the typical salts exhibit strongly polar properties and the term "salt like" is in itself a fair definition of the term polar. The contrast between the properties of this class of substances and such compounds as silicon tetrachloride or carbon bisulfide, as to melting point, volatility, latent heat of fusion and evaporation, and ability to ionize in aqueous solutions is most striking. Owing to their relatively high melting point comparatively little is known as to the properties of salts in the liquid state but there is abundant evidence to show that they are themselves more completely ionized than water and that in general they are miscible with one another over a wide range of concentrations.

The equilibrium diagram for those salts which are not decomposed at temperatures necessary to fuse them does not differ fundamentally from that of any other one-component system, such as water. The triple point is located at a much higher temperature and the pressure of the vaporized salt, even at this temperature, is usually so small as to make recognition and measurement of it difficult. The salts of ammonium are exceptional in their relatively low melting points, great volatility and appreciable dissociation at moderate temperatures. Solid ammonium chloride, for example, when heated to 340° gives a vapor pressure of 778 mm. without forming a liquid phase. In this salt, however, the large vapor pressure is due in part to the dissociation of the vapor into NH_3 and HCl, but since the composition of the vapor obtained by heating the salt must be the same as that of the salt itself the system can be treated as a one-component system.

Those salts which are decomposed with the formation of a new solid phase when heated can not be treated as one-component systems since it is not possible to express the composition of either the new solid or the resulting vapor phases in terms of the pure salt. A large number of the nitrates, sulfates and carbonates, especially of the more weakly basic elements, is included in this class.

The diagrams for certain salts are further modified by the formation of more than one crystalline form. In such cases there must be an additional triple point. A suggested form of diagram for a salt of this type, which does not undergo appreciable

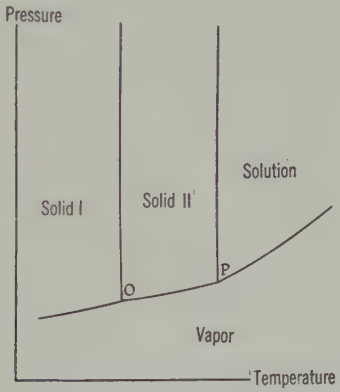

FIG. 4.—Ideal diagram for a di-morphic salt.

decomposition at its melting point, is represented by Figure 4, in which O and P represent triple points.

Peculiarities of Salt Solutions. Aqueous solutions of soluble salts, with which this volume is especially concerned, are almost without exception "strong electrolytes." This designation has been applied to those substances which show a large (as much as fifty percent) dissociation, as determined by conductance methods, if the total concentration is not greater than half molal. The use of the conductance method is based upon two assumptions, first, that the conductance depends upon the product of the concentrations of the ions and their respective mobilities, and second, that the mobilities do not vary with the concentration. It has been shown by Lewis,[1] however, that the mobilities of the ions

[1] Lewis, *J. Am. Chem. Soc., 34,* 1861 (1912).

in solutions of strong electrolytes do vary with the concentration, which seems to be a necessary consequence of the fact that the ions are more or less hydrated and the mass law requires that the degree of hydration, and therefore the mobility, should vary with the concentration. Lewis [2] has also pointed out that the meaning of the term degree of dissociation lacks definiteness, for although dissociation implies actual separation of the resulting ions, it is not possible to specify what degree of separation is required to give the products the properties of true ions. It is also well established that changes in the dissociation of strong electrolytes with the dilution are not in agreement with the mass law but that these changes depend largely upon the charge on the ion, being greater for uni- than for di-valent ions, and further that the properties of one ion are affected by the presence of all the other ions which the solution contains.

Owing to these difficulties the significance of the so-called degree of dissociation, as determined by conductance methods, should be seriously questioned. It seems more rational to attempt to determine what might be called the effective concentrations of the ions by measurement of the changes in the thermodynamic properties of the solution, which result from changes in the total concentration of the electrolyte. Lewis [3] proposed to determine what he called the thermodynamic degree of dissociation or the "activity coefficient." He defined the molecular activity as the relative fugacity or effective concentration as compared with the fugacity of the molecular species concerned at some standard state, which could be chosen arbitrarily. The activity coefficient of the ionized electrolyte was also defined as the mean activity of the ions to which it gave rise, when determined by methods which depend upon such properties as changes in the vapor pressure of the solvent, solubility, electromotive force, etc. None of these methods gives definite information as to the actual concentrations of the ions present, but there is ample justification for adopting as a working hypothesis the theory elaborated by Debye [4] and others, which assumes that strong electrolytes are totally dissociated at all concentrations, but that the actual effective concentrations of the ions present are greatly reduced by the

[2] Lewis and Randall, *Thermodynamics*, p. 328 (1923).
[3] Lewis, *J. Am. Chem. Soc.*, *34*, 1931 (1912).
[4] Debye, *Rec. Trav. Chim.*, *42*, 597 (1923).

attractive force which exists between the ions themselves and also between the ions and molecules of solvent.

The determination of the activity coefficients of the more important electrolytes for a number of concentrations should make it possible to calculate the important properties of solutions of these electrolytes with a degree of assurance which is not possible at present. The limited amount of data available in 1923 was used for the calculation and compilation of a table of such coefficients by Lewis and Randall.[5] Many additions to this table are now possible as the result of the activity of a number of workers. In the absence of a more comprehensive table of such data it is often necessary to revert to the earlier methods of making such calculations, namely, those based upon conductance data.

The treatment of the system water-soluble salt is greatly simplified by the slight volatility of the salt component, for with but few exceptions it can be assumed that the vapor phase in equilibrium with the solution consists of water vapor only. A further simplification arises from the fact that only a single[6] liquid phase is ordinarily present in such a system. This fact is undoubtedly dependent upon the close similarity of the components of this type in that both are strongly polar. In general additional liquid phases are not formed unless the two components differ greatly as to polarity. Further peculiarities of salts, such as the formation of hydrates and of solid solutions, will be discussed in Chapters III and VI.

Concentration as a Variable. The addition of a soluble salt to water yields a two-component system, for it is not possible to express the composition of the resulting solution in terms of either salt or water. As the solubility of the salt decreases, the properties of the solution must approach those of pure water, and if the solubility is zero there is no true equilibrium, and the mixture can be treated as two independent one-component systems. The errors which result from the treatment of systems composed of water and a very slightly soluble salt as independent one-component systems can usually be disregarded. If this were not so it would be necessary to consider the containing vessel as a component of all systems.

[5] Lewis and Randall, *Thermodynamics,* p. 382 (1923).

[6] A system which yielded two liquid phases was obtained by the writer when working with solutions containing large concentrations of K_2CO_3 and smaller concentrations of NaCl.

The properties of water may be made to vary by the addition of soluble substances just as they may be varied by changing the temperature and pressure. Since the amount of added substance can be varied continuously, between zero and the amount required to saturate the resulting solution, these properties can be made to vary between certain limits, and hence the concentration of the dissolved substance constitutes a third variable, whose significance is similar to that of pressure and temperature. Assuming for the present that the salt is not appreciably volatile and that it does not form hydrates or solid solutions with solid water, the only difference to be considered in comparing the properties of the system water with those of the system water and salt depend upon the differences between the properties of water and those of the salt solution. In considering these differences there are three variables to take into account, namely, pressure, temperature and concentration.

Vapor Pressure Curves of Salt Solutions. When a soluble salt is added to water in increasing amounts its fugacity is reduced from that of pure water to that of water in a saturated solution. Simultaneously the fugacity of the salt in the solution is increased from zero to that of the salt in the saturated solution, which must be the same as that of the pure salt because the solid and liquid are in equilibrium with each other. Since a reduction in the fugacity of water necessarily involves a reduction in vapor pressure, the vapor pressures of salt solutions must be less than those of pure water at the same temperature. If the relation between vapor pressure and temperature, for a salt solution of constant composition, be represented by a curve, the latter must assume a form similar to OA of Figure 2 but must be located some distance below, although not necessarily parallel to, OA. If the concentration of the solution is made still greater, the corresonding curve must be located still further below OA. Since, however, the reduction in fugacity is dependent upon the total concentration of all the molecular species derived from the added salt it is affected by the factors which affect the dissociation and hydrolysis of the latter, and hence is not proportional to the concentration of the added salt.

These facts may be represented graphically by adding to Figure 2 a third axis, placed at right angles to the plane including the pressure-temperature axes, which represents the ratio of salt to

water in the system. This has been done in Figure 5, in which OA is the pressure-temperature curve for pure water and O_1-I, O_2-II, O_3-III, etc., are corresponding curves for solutions of increasing salt concentration. The diagram indicates that it is possible to choose certain successive points on the curves O-I, O_2-II, etc., representing the same values for a chosen temperature or a chosen pressure. Unlike the system liquid water-water vapor,

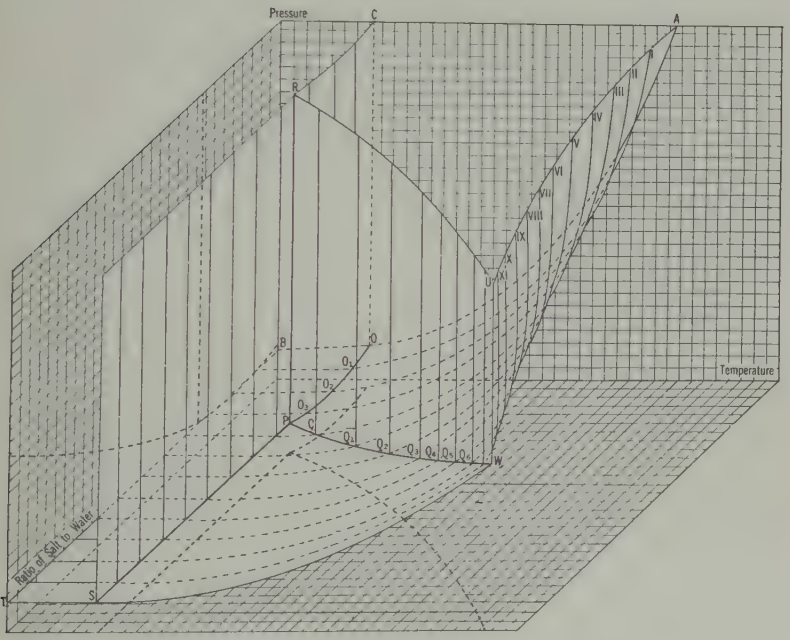

FIG. 5.—Pressure-temperature-composition diagram for the system salt-water.

represented by OA, fixing the temperature does not necessarily fix the pressure. It is also obvious that by drawing a sufficient number of these curves, a warped surface, representing in its entirety the system water vapor-salt solution of variable composition, can be represented. The curves here given are not based upon actual experimental work but outline roughly a probable form of such a surface.

The facts stated above are in agreement with the fact that the fugacity of water in the solution is fixed by an equation involving variable values for pressure, temperature and concentra-

tion, while that of water vapor is fixed by an equation involving variable values for pressure and temperature only. Since the two phases are in equilibrium the pressures, temperatures and fugacities of the two phases must be identical, and hence the entire system involves only four variables, which are concerned in only two equations, and therefore such a system must possess two degrees of freedom. They are comparable to pure water existing as a single phase.

The Freezing Point Curve. If the temperature of the system water vapor-salt solution of fixed concentration is sufficiently reduced, and if the chosen value of the concentration is not too great, solid water must finally separate. The temperature at which this will take place constitutes a limiting value, which cannot be further reduced unless the concentration of the liquid phase is also changed. If the points representing such values for a series of solutions, each of which has a different concentration, such as points O_1, O_2, etc., of Figure 5, are connected, a "freezing point curve" will be obtained. All the points on such a curve represent equilibria between water vapor-salt solution-ice, in which the fugacity of water in the three phases must be the same. The addition of ice to the system solution-vapor introduces an additional requirement in the form of an equation indicating the effect of pressure and temperature upon the fugacity of ice. Since this equation adds no new variables there are now four variables and three equations and hence the system has but one degree of freedom. One of the limiting values of this curve must correspond to the triple point of water, for if the concentration of the salt solution is gradually reduced to zero the fugacity of water in the solution must attain the value which it has in pure water, when the latter is in equilibrium with ice and water vapor.

The equilibria represented by points on this curve are possible only because the extent to which the fugacity of ice is reduced by a given reduction in temperature can be made equal to that to which the fugacity of water in the salt solution is reduced by the combined effect of the same reduction in temperature and the presence of a certain amount of salt. This would not be possible unless the rate at which the fugacity of ice is reduced by decreasing temperature exceeds the rate at which the fugacity of liquid water is reduced by the same means. The difference in this rate is known to depend upon the difference between the

heat content of water in liquid and solid forms, and therefore upon the latent heat of fusion of ice when supercooled to the equilibrium temperature. The rate at which the fugacity of liquid water is reduced by adding a salt depends chiefly upon the sum of the molecular species derived from the salt. If water and salts were non-polar substances the relation concerned could be expressed by the equation

$$\frac{d\ln N}{dT} = \frac{\Delta H}{RT^2}$$

in which it is assumed that the total pressure is constant, that N represents the mole fraction of water in the solution, T the freezing point of pure water, ΔH the latent heat of fusion of ice and R the gas constant. This equation states that in this equilibrium a decrease in the molal concentration of water in the solution, which is necessarily associated with an increase in the concentration of salt in the solution, can be offset by a decrease in temperature, the magnitude of which depends solely upon certain of the physical properties of water, not upon those of the salt. It was first derived by Schröder [7] as a result of a study of changes in osmotic pressure due to the presence of varying concentrations of solute; it can be more easily derived from a study of the factors affecting the fugacity of such solutions.[8] From the integrated form of this equation, namely

$$\ln N = \frac{\Delta H}{R} \cdot \frac{T' - T}{T'T}$$

in which R is the gas constant expressed in calories, T′ the freezing point of water, T that of a solution in which the mole fraction is N, it is possible to calculate the numerical value of $T' - T$ or ΔT, that is the reduction in the freezing point of water resulting from the presence of one mole of solute per 1000 grams of water. If one mole of a substance, which is assumed to undergo no dissociation and no hydrolysis, is dissolved in 1000 grams of water, the mole fraction would be 0.9823. Substituting this value for N, 1428 for ΔH, 1.9885 for R, 273 for T′ and introducing the factor 2.303 to change from natural to common logarithms, we obtain for T the value 271.175 and hence

[7] Schröder, *Z. physik. Chem., 11,* 449 (1893).
[8] See Lewis and Randall, *Thermodynamics,* p. 229 (1923).

$\Delta T = 1.825°$. This constant can be used to calculate the corresponding value for ΔT for any salt whose degree of dissociation is known. For a univalent salt, the average degree of dissociation of which at 0.1 molal concentration has been calculated to be 0.84, ΔT has the value 3.358.

The Solubility Curve. If the concentrations of dissolved salt in the liquid phase of the system water vapor-salt solution of constant composition are sufficiently large, solid salt rather than ice will begin to separate when the temperature is sufficiently reduced. The forms of the curves representing such equilibria are indicated by Q-IV, Q-V, etc., of Figure 5. The temperature at which the salt separates cannot be varied unless the temperature change is also associated with a change in concentration because an additional phase has separated, and the system has become monovariant. When these points are connected they form a "solubility curve" for the salt concerned, as represented by P, Q, Q_1, etc., of Figure 5 because the amount to which the fugacity of the solid salt is decreased by a given decrease in temperature can be made equal to the amount to which the fugacity of the salt in the solution is decreased by the combined effect of the given decrease in temperature and some specific decrease in the concentration of the solution with respect to the salt. The difference between the rates at which the fugacity of the solid salt and the dissolved salt are reduced by decreasing temperature depends upon the difference in the heat content of the salt in these forms; it is the same as the heat of fusion of the salt at the equilibrium temperature. The expression already used, which determines the change in the freezing point of the solvent with the concentration of the solvent, also determines the change in the solubility of the solute with the temperature, provided d ln N has reference to the mole fraction of the solute in the saturated solution, T′ the melting point of the solute and ΔH its latent heat of fusion. The temperature of fusion of most salts is very high as compared with that of water, and measurements of the heat of fusion of salts supercooled to the extent represented by the temperature at which solubility measurements are usually made are scarcely possible. The desired constant can be ascertained by measuring the heat absorbed when a mole of the salt is dissolved in a very large amount of the nearly saturated solution. Very few measurements of this kind

have been made.[9] The heat of solution as ordinarily determined, that is by dissolving the salt in a large amount of pure water, may differ both in sign and magnitude from the quantity which is related to the effect of temperature upon solubility.

The Eutectic Point. The preceding paragraphs indicate striking points of resemblance between freezing point and solubility curves. It was first pointed out by Guthrie[10] that the freezing-point curve can be considered a solubility curve in which liquid salt is saturated with ice, and the solubility curve can be considered a freezing-point curve in which solid salt is made to freeze from water by reducing the temperature.

If both curves are sufficiently prolonged in the direction of decreasing temperature they will intersect, and the resulting system will consist of water vapor-solution-ice-salt. The temperature at which they intersect must represent the lowest point, P of Figure 5, at which the liquid phase can exist, for any attempt to remove heat from the system will transform the liquid into two solid phases. Further, the composition of the solution is fixed, for any attempt to change it would necessitate supersaturation with respect to either ice or salt. This point therefore has peculiar properties and is known as the cryohydric point. The terms cryohydric temperature and cryohydric composition are also in general use. The more comprehensive term eutectic is used to designate systems in which any two solids, a liquid of fixed composition and vapor are in equilibrium. The peculiarity of cryohydric systems is that one of the two solids is ice.

Owing to the high melting point of most salts as compared with ice the temperature-composition interval within which the system ice-solution-vapor can exist, which determines the length of the freezing point curve of ice, is small as compared with a similar interval for the system salt-solution-vapor, which determines the length of the solubility curve of the salt.

The solid mixture which separates at the eutectic point when heat is removed from the system must have a definite composition although a true mixture. It usually has a fine grained structure but can be resolved into its two component solids by moderate

[9] See, however, the work of Randall and Bisson, *J. Am. Chem. Soc., 42,* 347 (1920).

[10] Guthrie, *Phil. Mag., 18,* 117 (1884).

magnification. When first obtained by Guthrie (*l. c.*) such mixtures were taken for compounds.

It can be shown that there is only one set of temperature, pressure and composition values at which such systems can exist. The fugacities of water in its three forms and of salt in its two forms must have identical values. The required conditions are summarized in the following equations, in which P is the total pressure and T the temperature of the entire system, C the concentration of salt in the liquid phase and Fu the fugacity of water or salt in the different forms.

$$f(P.T.Fu\ \text{water vapor}) = 0$$
$$f(P.T.C.Fu\ \text{water in solution}) = 0$$
$$f(P.T.Fu\ \text{solid water}) = 0$$
$$f(P.T.Fu\ \text{salt in solution}) = 0$$
$$f(P.T.Fu\ \text{solid salt}) = 0$$
$$\text{Fu water vapor} = \text{Fu water in solution}$$
$$\text{Fu water in solution} = \text{Fu solid water}$$
$$\text{Fu salt in solution} = \text{Fu solid salt}$$

Since there are eight variables, namely P, T, C and five values for Fu, and eight equations, five of state and three of equilibrium, only one set of variables can satisfy all equations.

The introduction of air as an additional component affects the form of the two equilibrium curves which have been considered, and therefore the location of the eutectic point, but slightly. The diagram can be used to represent such systems under atmospheric conditions without appreciable error, provided it is remembered that the pressure axis represents partial pressures of water vapor rather than total pressure.

The System Ice-Salt Solution. If the pressure upon the system represented by the eutectic point is increased the total volume which it occupies must decrease and the vapor phase will disappear since it is affected by such a change to a much greater extent than solid or liquid phases. Since disappearance of this phase does not change the number of variables but reduces by one the equations connecting them, the system must acquire one degree of freedom. Hence the system ice-solid salt-solution can exist in equilibrium when a number of different but properly correlated values are assigned to the three variables P, T and C. In order to represent these systems a third curve, which starts at the

eutectic point, should be shown on the diagram representing the system. By analogy with the water-ice system the factors which determine the form of this curve should be the volume change and the heat change which take place when mixtures of ice and salt, in the proper proportions, unite to form a solution of some definite composition. The relation between the changes in pressure and temperature necessary to maintain equilibrium in such systems can be ascertained by use of the Clapeyron equation, that is, depends upon the ratio between the heat change and the volume change. Since the former magnitude is very large as compared with the latter a very small change in temperature is required to offset a large change in pressure. Furthermore, since a very large change in pressure is needed to affect the solubility of a solid to an appreciable degree the curve in question can be represented with sufficient accuracy for most purposes by a straight line, PR of Figure 5, parallel to the pressure axis, although it is neither straight nor parallel to that axis. It should be noted that the pressure here referred to is the total pressure, whereas for the curves OA and OB it represents the partial pressure of water vapor.

The System Ice-Salt-Water Vapor. A fourth system consisting of three phases in equilibrium, that is ice-salt-water vapor, should be considered. Since the salt is not a component of either the vapor or the solid phase it is in no real sense a part of the system and the addition of solid salt to the system ice-water vapor has no effect upon it provided the pressure of the water vapor is less than that of a saturated solution of the salt. If, however, it is desired to complete the diagram it may be assumed that the solid salt is added to the system represented by the point P, which should correspond to movement of this point in a straight line parallel to the concentration axis as far as the limits of diagram at S. In addition the curved line TS has been located by drawing lines from points on the lower portion of the BO curve parallel to the concentration axis until they intersect the plane marking the limits of the diagram. Similarly the curved line SW has been located by drawing lines from points on the PW curve parallel to the concentration axis.

The Complete Diagram for the System. The four curves which meet at the eutectic point represent three-phase, univariant systems and the six surfaces connecting these curves must repre-

sent two-phase bivariant systems. The surface AOPWU represents equilibria between water vapor and solutions of variable composition, the surface UWPR equilibria between solid salt and saturated solution and the surface PRCO equilibria between saturated solution and ice. These surfaces, together with the plane of the pressure-temperature axis define the lower limits of a space representing the trivariant system, solution. Similarly the space defined by RPWU, WPS and RSP might be expected to represent the trivariant system solid salt, that defined by COPS, BOST and the planes defined respectively by the pressure-temperature and pressure-concentration axes should represent the trivariant system ice, and all of the space below the surface ABTSW the trivariant system water vapor. The actual significance of the spaces thus defined is very different from that of the space representing unsaturated solutions because ice and salt in the solid state do not form homogeneous mixtures, and salt is not appreciably volatile at the temperatures which have been assumed. Since there are no concentrations to consider in either the solid or the gaseous phases the phases to which these spaces correspond must represent two- or three-phase mixtures. Points included within the space above WPS actually represent mixtures of solid salt and saturated solutions corresponding to points on the URPW surface, and points within the space below PSW represent solid salt and water vapor. This is a necessary consequence of the fact that no single phase, which has a composition corresponding to points within these spaces can exist at the temperatures and pressures concerned.

Derivation and Use of the Phase Rule. Certain relations between the degrees of freedom and the phases concerned in the systems which have been discussed have been pointed out. A review of the statements will show that the degree of freedom of all systems discussed in Chapter I can be found by subtracting the number of phases present from three, that is, from the number of components plus two, while the degree of freedom of all the systems discussed in Chapter II can be found by subtracting the number of phases from four, which is also the number of components plus two. It can be shown that this relation represents a universal rule. Although the peculiar properties of salt and water made it justifiable to make a number of assumptions, which greatly simplified the possible changes in such systems, it can be shown that in any kind of system whatever the addition of a

component increases the number of variables to be considered by one more than the number of additional equations, which must be used to express the relations which exist between the variables. This rule can be used advantageously in discussing complex systems composed of water and two or more salts for by its use it is possible to indicate with certainty some of the equilibria which are possible and some which are impossible. The chief difficulty in making use of the rule is to ascertain correctly the number of components concerned. Although this question will be considered in detail in subsequent chapters it may be noted here that the components of a system must be chosen in such a manner as to comply with three requirements. Each component must exist in at least two of the phases of the system concerned; the concentration of each component must be capable of being varied continuously in at least one of the phases present; and the components used must be so chosen that the fewest possible are employed in expressing the composition of all the phases present.

Water and Salts Whose Solubility is Infinite. In the preceding paragraphs the series of changes which result from the addition of a soluble salt to water, starting at its triple point, have been discussed. It would have been equally logical to have considered the changes which result from the addition of water to the salt, starting at the triple point of the latter, but owing to the high melting point and slight volatility of most salts it is more difficult to obtain experimental data for this portion of such systems.

The diagrams for those salts which are not decomposed at their melting points also consist of three curves meeting at a triple point, whose temperature is almost identical with the melting point of the salt under atmospheric conditions, and whose pressure, at least for the great majority of salts, is some very small value. The form of the three curves is similar to the form of those of the water system. If the solubility of the salt increases indefinitely the solubility curve must connect the eutectic point with the triple point of the salt. Ordinarily such curves are not followed beyond the boiling point of the saturated solution, but if determinations are made in closed vessels so that the pressures may be increased above that of the atmosphere, values for higher temperatures may be obtained. Guthrie [11] was able to obtain a

[11] Guthrie, *Phil. Mag., 18,* 114 (1884).

sufficient number of points on the solubility curve of potassium nitrate to show that it was continuous and Etard [12] obtained data leading to similar conclusions for silver nitrate, sodium nitrate, thallium nitrate, potassium chlorate and potassium dichromate. Continuous but multiple solubility curves, each portion of which represented saturation as to a differently hydrated solid, were obtained by Morey [13] for (1) $K_2Si_2O_5 . H_2O$ and $K_2Si_2O_5$ and (2) $K_2SiO_3 . H_2O$, $K_2SiO_3 . \frac{1}{2}H_2O$ and K_2SiO_3.

The vapor pressures of such solutions must increase from very small values at the eutectic point to large values but must ultimately attain the very small values of the pure salt at the triple point, and hence must pass through a maximum. Very few measurements of the vapor pressures of solutions saturated above 100° have been made but Cohen and Smits [14] obtained measurements with solutions of silver nitrate which showed a clearly defined maximum of 1010 mm. at 170°. Solutions of this type must exhibit two sets of temperature and concentration values which give the same vapor pressures, and therefore two different boiling points. The values found for saturated solutions of silver nitrate were 133° and 191°. At first sight this would seem to involve a contradiction to the phase rule but the difficulty disappears if the method used in deriving this rule is recalled, for it is mathematically possible to obtain in certain cases more than one set of values which will satisfy the variables which appear in equations concerned.

Critical Phenomena of Salt Solutions. It seems probable that all salts should exhibit critical phenomena similar to those of water, provided they do not decompose and form two component systems before the requisite temperature and pressure are reached. If this is true, certain mixtures of such salts and water should also show critical phenomena, namely, the peculiarity that the liquid and vapor phases not only have the same percentage composition at certain properly correlated pressures and temperatures but also are identical in all of their properties. It was shown by Smits [15] in discussing the critical phenomena of two component systems generally that two classes could be distinguished.

[12] Etard, *Ann. Chim. Phys.*, (7), *2*, 503 (1894).
[13] Morey, *J. Am. Chem.*, *39*, 1208 (1917).
[14] Cohen and Smits, *Kon. Akad. Wetts*, Amsterdam, 10, 355 (1901).
[15] Smits, *Z. physik. Chem.*, *51*, 194 (1905).

If the critical temperatures of the two components greatly exceed the temperatures of their respective triple points the series of points representing the critical constants of mixtures of such components should form a continuous curve on the temperature-concentration diagram connecting the critical points of the pure components. A projection of such a hypothetical system on the plane of the pressure-temperature axes is shown in Figure 6, in which K_1 and K_2 represent the critical constants of the two components, M_1 and M_2 their respective triple points and the line $OabcM_2$ the continuous solubility curve. The vapor pressures of solutions saturated at the temperatures concerned are in all cases less than the pressures corresponding to similar temperatures on the critical curve

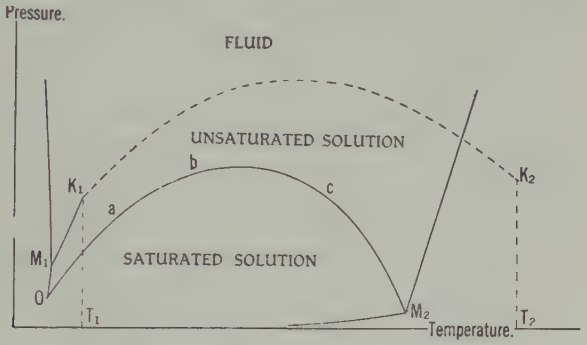

FIG. 6.—Ideal diagram for a pair of salts in which the critical constants change continuously.

and all the solutions which exhibit critical phenomena are unsaturated. All the systems composed of salt and water, which show a continuous solubility curve, are illustrations of this class. The fact that critical phenomena are not met with at any point on such curves and that the critical temperatures of the pure components have been assumed to exceed those of their triple points makes it necessary to assume that for the entire range of concentrations the critical curve is above the solubility curve.

If the differences between the two sets of constants are not so great and if the solubility of the less volatile component is small these curves may intersect as represented in Figure 7. Between K_1 and p and again between q and K_2 the critical curve is that of the unsaturated solutions, but between p and q the liquid phase of the critical curve is supersaturated, and this portion of the curve

actually represents a metastable system. At p and q, which Smits called critical end points, the vapor pressures of the saturated solutions and the critical pressures are identical. Between the temperatures T_2 and T_3, therefore, critical phenomena are not possible, and it is possible to pass from the region in which solid-saturated solution-vapor exists to one in which solid-fluid exists without any easily recognizable evidence of the transformation. The system sodium sulfate-water, which will be discussed in the next chapter, illustrates a system of this type.

Systems with Di- and Tri-Morphic Salts. The different solid modifications of dimorphic and trimorphic salts possess different fugacities and therefore different vapor pressures and

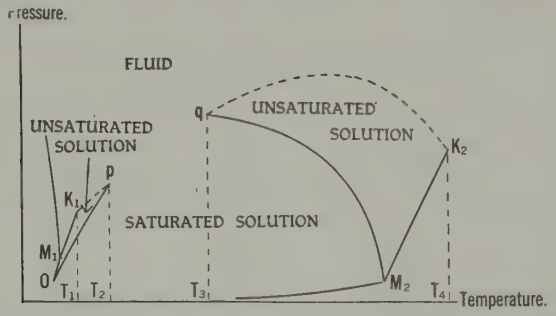

FIG. 7.—Ideal diagram for a pair of salts in which the critical constants show a discontinuity.

solubilities. Hence the solubility curves of such salts must show breaks at those temperatures at which one solid form changes into another. The concentration-temperature curve for the system water-ammonium nitrate,[16] represented in Figure 8, shows in addition to the eutectic point three such breaks corresponding to the points C, D and E. They are known as "inversion points" and as they represent four-phase systems they are invariant. They must also represent points from which four curves representing univariant systems originate, although only two such curves are shown on the diagram. Taking the point C as an illustration, the curve BC represents the solubility curve for Solid I and CD the corresponding curve for Solid II. A third curve, which represents Solid I-Solid II-solution has a form which is determined by the heat change as compared with the volume change when Solid I

[16] Roozeboom, *Rec. Trav. Chim.*, *8*, 267 (1889).

and solution of some specific composition, form Solid II and solution of a slightly different composition. As the heat change is presumably large as compared with the volume and composition changes this curve should extend from C upwards and should be roughly parallel to the pressure axis. A fourth curve represents

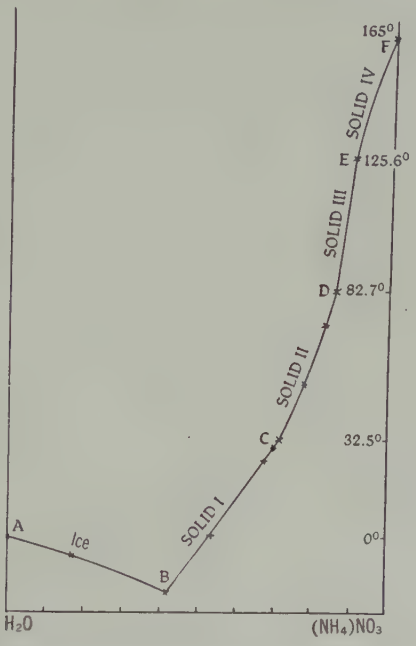

FIG. 8.—Concentration-temperature diagram for the system ammonium nitrate-water.

Solid I-Solid II-vapor. If it is assumed that neither solid is appreciably volatile the form of the curve is determined by the difference between the heat and volume changes when Solid I forms Solid II. If one or both of the solids are appreciably volatile the composition of the vapor is also of significance. The two additional curves which originate at the points D and E are similarly determined.

Chapter III.

Systems Derived from Water and a Single Salt Which Forms One or More Hydrates.

Solid Hydrates. The only definite knowledge concerning the composition of hydrated salts is derived from those which can be made to assume a crystalline form. The formation of crystals demands a specific spatial arrangement of the atoms or groups of atoms concerned held in place by fairly rigid restraints, and also demands compliance with certain volume relations between the atoms or groups of atoms concerned. These facts increase greatly the difficulties in ascertaining the nature of the forces concerned in the formation of hydrated salts.

The application of X-ray analysis to the study of crystals has shown that the polar relations of simple salts, such as sodium chloride, are retained when they assume a crystalline form. Each atom of chlorine associated with its negative charge, is equidistant from six of sodium, each associated with its positive charge, and also each sodium ion is equidistant from six chlorine ions. It seems probable also, as suggested by Langmuir,[1] that the atoms of more complex salts such as $NaNO_3$ and K_2CrO_4 are associated in the formation of groups, whose formulæ are identical with those of the corresponding ions found in liquid solutions. Unfortunately but few hydrated salts have been successfully studied by the methods of X-ray analysis but it seems probable that the polar structure of the ionic constituents is also maintained in solid hydrated salts.

The large number of salts which form hydrates and the number of different hydrates which many salts are capable of forming clearly indicate that the formation of these compounds is not related to the polar valencies of the compounds concerned. It seems necessary therefore to assume the existence of certain additional bonds of affinity which hold together the salt and water molecules.

[1] Langmuir, *J. Am. Chem. Soc., 38,* 2234 (1916).

This feature is included in the theory of Werner,[2] which postulates that one or both of the component ions, especially the cation, are made up of a central atom acting as a nucleus, which holds in combination certain other atoms by primary valencies and certain atoms or atomic groups, such as NH_3, H_2O or NO_2, by auxiliary valencies. According to this theory the total number of primary and secondary valencies which the central atom can exert is fixed; it represents the "coordination number" which is a characteristic property of the atom concerned. Although the formulæ of a large number of hydrated salts are in agreement with the set of coordination numbers which Werner assigned the more important salt-forming ions, it is impossible to correlate all of these with any simple series of coordination numbers. Werner found it necessary, therefore, to assume the existence of still a third type of valence which held some or all of the water molecules in a loose combination with the complex ion, the latter acting as a unit. No definite limits were assigned to the number of molecules of water which could be held in this manner.

A second suggestion which has an important bearing upon the formation of hydrated salts is found in the theory of Abbegg and Bodländer,[3] which assumes that a relation exists between the capacity of the different ions to form hydrates and the electro affinity of these ions. It assumes that the weak ions, especially the ions of those metals which are low in the electropotential series, are associated with an excess of positive or negative charge, which they can share with a "neutral part," such as a molecule of NH_3 or H_2O, the whole forming a more stable complex than the original ion. Although the theory is somewhat vague it emphasizes what seems to be a well-established fact, namely, that the weak cations are more frequently concerned in the formation of complex ions, of which the hydrates are examples, than the strong ions.

The more recent ideas as to the nature of valence and chemical affinity developed by Lewis[4] are comprehensive enough to readily account for the numbers and the complexity of hydrated salts. The sulfate ion, for example, possesses twelve pairs of electrons, each capable of attaching to itself a water molecule

[2] Werner, *Z. anorg. Chem., 3,* 294 (1893).
[3] Abbegg and Bodländer, *Z. anorg. Chem., 20,* 453 (1899).
[4] Lewis, "Valence and Structure of Atoms and Molecules," Chem. Catalogue Co. (1923).

or a chain of such molecules. Similarly the nitrate ion possesses ten such pairs and the halogen ions four. It is also possible that certain of the simple ions may be more or less polar, that is, as the result of a lack of symmetry in the positions assumed by the electron pairs in the molecule, certain portions of the ion may show an excess of positive or negative charge. Such regions might serve as points of attachment for the dipolar water molecules. Of the two methods of attachment here suggested the former represents the stronger; it is not improbable that in certain hydrates the more firmly bound water is attached by electron pairs and the less firmly bound by electrostatic forces. Such an assumption brings the theory into harmony with some of the ideas of the theory of Werner. In general the ease with which water can be removed from hydrated salts indicates that it is electrostatic forces which are chiefly concerned in the formation of these compounds. The almost unlimited range of possibilities as to the formation of hydrated salts, which the Lewis theory offers, finds many limitations through the forces which are concerned in the formation of crystals when applied to the formation of solid hydrates.

Hydration of Salts in Solution. The large amount of heat liberated when certain anhydrous salts, which form solid hydrates, dissolve and the color changes associated with the solution of the anhydrous salts of certain elements, like copper and cobalt, are difficult to explain unless it is assumed that these salts exist in hydrated form in solution. The changes in certain of the physical properties of salt solutions, notably their viscosity, surface tension, mobility of the ions present, rates at which the vapor pressure and the closely related freezing-point depression change, which result from varying the concentration of the salt, also indicate that both the ions and the ionized salt are hydrated to a greater or less degree. Still more conclusive evidence is obtained from a study of the changes in the concentrations of the ions present which take place when an electric current is passed through solutions containing a non-electrolyte as a reference substance in addition to an electrolyte.[5]

Many methods have been used in attempting to measure the degree of hydration of the different ions. It is generally assumed

[5] Washburn, *Technological Quarterly of Mass. Ins. of Technology,* No. 3, Sept. 1908.

in these investigations that the percentage of hydration decreases with increased concentration of the salt, as required by the mass law, and hence that the concentration of the free water molecules decreases less rapidly than the increased salt concentration demands, and therefore changes the value of the physical property measured abnormally. In using such methods it is not possible to distinguish between the number of molecules of water held by the ion in question and the magnitude of the constant which fixes the proportion of ions which are hydrated. The degree of hydration found indicates the average number of moles of water held by all the ions present. A summary of the results obtained by these methods by Fricke [6] shows a fair qualitative agreement and he found it possible to arrange a number of the more common ions in a series with respect to their degree of hydration. A more recent survey of the data relating to the viscosity of solutions of strong electrolytes by Sugden [7] led him to advance the theory that only the cations are hydrated and that certain anions depolymerize the solvent molecules and produce "negative hydration." His theory is supported by a large amount of experimental work.

The System Solid Hydrate-Vapor. Although a number of anhydrous salts can be treated as one-component systems none of the hydrated salts can be so treated. Certain of them have true melting points and the composition of the liquid and solid phases can be expressed in terms of the same compound, but heating the pure solid usually yields a new solid and a liquid or vapor, and an additional component is needed to express the composition of the resulting system. Under ordinary conditions most salts are not at equilibrium in the solid state unless associated with a vapor phase, which consists of water vapor and negligible amounts of the salt itself. Such equilibria, like all true equilibria, must represent a certain stage in a process which can be expressed by means of a chemical equation. The general form of the expression must be either

$$MA.xH_2O \longrightarrow MA(x-y)H_2O + yH_2O \text{ (vapor) or}$$
$$MA.xH_2O \longrightarrow MA + xH_2O \text{ (vapor).}$$

In both systems there are two solids and one vapor phase and since both are two-component systems they must have one degree

[6] Fricke, *Z. Elektrochemie, 28,* 169 (1922).
[7] Sugden, *J. Chem. Soc., 128,* 174 (1926).

of freedom. The effect of varying pressure and temperature upon such systems can therefore be represented by means of a curve similar to OA of Figure 2. The form of such curve can be calculated by means of the van't Hoff equation if the increase in the heat content and the volume of the system due to the reaction are known. The integrated form of this equation, namely

$$\ln p = \Delta H \div RT + B$$

in which B is the integration constant, shows that the ratio between the logarithm of the pressure and the reciprocal of the absolute temperature, at which the two solids and the liquid are in equilibrium, is a constant. It is customary therefore to judge of the accuracy of experimental measurements of such equilibria by plotting log p against T and noting to what extent the resulting graph agrees with a straight line. It should be noted, however, that this method is reliable only to the extent to which the fundamental assumptions of the van't Hoff equation, namely, that ΔH is constant and that water vapor is a perfect gas, are valid.

The data obtained in the investigation of the hydrates of copper sulfate illustrate these statements. The equilibria represented by

$$(1) \quad CuSO_4.5H_2O \longrightarrow CuSO_4.3H_2O + 2H_2O$$
$$(2) \quad CuSO_4.3H_2O \longrightarrow CuSO_4.H_2O + 2H_2O$$

have been measured with great care by Carpenter and Jelle.[8] Their results are shown graphically in Figure 9. The prolongation of these curves in the direction of lower pressures and temperatures probably gives an intersection before the absolute zero is reached. If so there must exist an invariant point consisting of the three solids and vapor. If the curves are prolonged in the opposite direction points should be reached at which a liquid phase appears, that is, a solution saturated with either $CuSO_4.5H_2O$ and $CuSO_4.3H_2O$ or with $CuSO_4.3H_2O$ and $CuSO_4.H_2O$. Both of these systems must be invariant. The former seems to have been realized by Etard[9] at a temperature of 106° and a pressure greater than 760 mm., since the boiling point of the saturated solution is known to be 104°. The only experimental data available which represent the equilibria

$$(3) \quad CuSO_4.H_2O \longrightarrow CuSO_4 + H_2O$$

[8] Carpenter and Jelle, *J. Am. Chem. Soc., 45,* 579 (1923).
[9] Etard, *Comptes Rendus, 104,* 1615 (1887).

are those of Lescoeur [10] for three temperatures only, all of them too great to be shown on Figure 9. There is also some evidence of the formation of solid $CuSO_4.6H_2O$ and $CuSO_4.9H_2O$ at temperatures below zero.

The dehydration of this salt has been assumed to take place in successive stages, each stage corresponding to the formation of a hydrate whose existence has been established and which contains the next smaller number of molecules of water. Each of

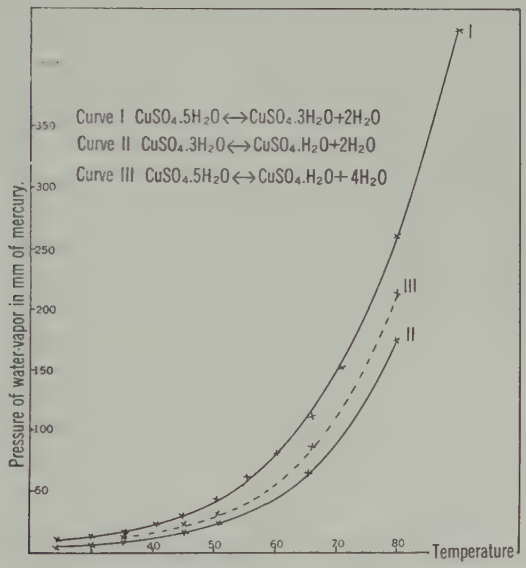

FIG. 9.—Pressure-temperature graphs for the hydrates of copper sulfate.

these hydrates should be capable of existence as stable solids within a certain range of pressures for each temperature, and the evidence seems conclusive that, for the salts thus far investigated, there is a correspondence between the position of each stable hydrate in such a series and the value of the two pressures between which it is stable. Presumably this indicates that the mean fugacity of the water molecules associated with each stage in the dehydration varies with the total number of water molecules in the solid which is dehydrated.

If the salt is placed under such conditions of pressure and

[10] Lescoeur, *Comptes Rendus, 102,* 1466 (1886).

temperature that more than one stage in the process of dehydration becomes possible, corresponding to such reactions as

$$(4) \quad CuSO_4.5H_2O \longrightarrow CuSO_4.H_2O + 4H_2O$$

the question arises as to whether the system will actually pass through the two intermediate stages in the process. Ostwald [11] cited many instances in which such processes took place in stages and announced his Law of Successive Reactions, which assumed that this represented the usual mechanism. It is obvious that since both processes involve typical chemical reactions they must be determined by (1) the free energies changes associated with these reactions and (2) the rates of speed with which they take place. This was recognized by Skrabal,[12] who made it clear that the appearance of metastable products was due to the greater rate of speed of the reaction producing them than that of the reaction producing stable products.

Using the data obtained by Carpenter and Jelle the free energy expressions for (1) and (2) at 25°, assuming that the activity of water is unity, are

$$(1) \quad -\Delta F = 2RT \ln 7.8 \text{ mm. Hg.}$$
$$(2) \quad -\Delta F = 2RT \ln 5.6 \text{ mm. Hg.}$$

Since (4) is the sum of (1) and (2) the expression for its free energy is the sum of those given, or

$$(4) \quad -\Delta F = 4RT \ln 6.7 \text{ mm. Hg.}$$

Similar calculations for (4) at temperatures of 35.17°, 45.07°, 65.10° and 80.08° give positive values for the equilibrium pressure of (4) at these temperatures. The curve to which they correspond has been plotted as a broken line on Figure 9. Although these calculations show that reaction (4) is possible at these temperatures this does not necessarily mean that the two solids concerned are stable within the range of pressure and temperature conditions represented by points of the curve. They should be metastable and react according to the equation

$$(5) \quad CuSO_4.5H_2O + CuSO_4.H_2O = 2CuSO_4.3H_2O.$$

Since the four reactions considered are thermodynamically possible the rates at which they take place must determine the sys-

[11] Ostwald, "Lehrbuch," Vol. II, 2, p. 445.
[12] Skrabal, *Z. Elektrochemie, 14,* 529 (1908).

tem which actually results. Carpenter and Jelle experienced no difficulty in causing reactions (1) and (2) to take place in both directions by slight variations in the water vapor pressures, presumably then the rate of (4) is exceeded by those of (1) and (2).

Aside from temperature the factors which determine the rates of such reactions are but poorly understood. In some cases they are clearly autocatalytic. Thus Lewis [13] found that the rate at which silver oxide formed silver and oxygen was greatly increased by the presence of metallic silver, and it is customary in measuring the equilibria of dehydration processes to insure the presence of amounts of both the solids present for the purpose of favoring the desired reaction. It is often difficult to ascertain with certainty the nature of the solids concerned in such measurements and to limit the reaction to the single one which it is desired to measure. For these reasons the accurate data available are meager.

The behavior of the hydrates of calcium sulfate illustrate some of the preceding statements. When $CaSO_4.2H_2O$ (gypsum) is rapidly heated to 180° in a loosely covered vessel it is almost completely converted into $CaSO_4.\frac{1}{2}H_2O$ (Plaster of Paris).[14] If heated more slowly, even at much lower temperatures, it can be completely converted into either one of two modifications of $CaSO_4$, a more reactive and more soluble form, and a less reactive less soluble form which is identical with the mineral anhydrite. It seems probable that the hemihydrate, at least up to temperatures of 90°, is metastable. Vapor pressure measurements were obtained by an indirect method by van't Hoff [15] for

(1) $CaSO_4.2H_2O \longrightarrow CaSO_4.\frac{1}{2}H_2O + \frac{3}{2}H_2O$
(2) $CaSO_4.2H_2O \longrightarrow CaSO_4$ (soluble form) $+ 2H_2O$

It is also possible to calculate from his data the equilibrium pressures for

(3) $CaSO_4.\frac{1}{2}H_2O \longrightarrow CaSO_4 + \frac{1}{2}H_2O.$

The data for the three reactions at four temperatures are as follows:

[13] Lewis, *Z. physik. Chem., 52,* 322 (1905).
[14] For experimental data relating to the preparation of Plaster of Paris see Keane, *J. Phys. Chem., 20,* 201 (1916).
[15] van't Hoff, *Z. physik. Chem., 45,* 288 (1903).

	25°	50°	75°	90°
Pressure in mm. of Hg for (1)....	9.1	50.0	210	446
" " " " " " (2)....	11.2	59.9	245	531
" " " " " " (3)....	20.9	81.8	389	896

The values for (3) are surprisingly large and, if the hemihydrate is assumed to be stable, the field representing it on the pressure-temperature diagram would exceed the limits of that representing the dihydrate. van't Hoff (*l.c.*, p. 268) was able to follow the curves representing (1) and (2) up to the point of intersection with the solubility curves. This point was attained for (1) at 107° and for (2) at 93°. These figures would make it necessary to assume that that portion of the solubility curve representing saturation with the dihydrate was located between those portions representing saturation with respect to the anhydrous salt and the hemihydrate respectively if the hemihydrate is not stable.

It is well known to manufacturers of Plaster of Paris that its setting power, which is due to the formation of the dihydrate, deteriorates on storage and that the rate of deterioration is greatly increased by the presence of a small amount of gypsum. This deterioration may be due to the reaction

$$(5) \quad 4CaSO_4.\tfrac{1}{2}H_2O \longrightarrow 3CaSO_4 + CaSO_4.2H_2O$$

a reaction for which gypsum might be expected to be a catalyst. The fact that the hemihydrate is never found naturally, whereas both gypsum and anhydrite are widely distributed minerals, furnishes additional evidence that it is metastable. The ease with which it can be made artificially must be due to the unusual rate of speed of (1) as compared with that of (2) and also the slow rates of reaction of (5).

The System Solid Hydrate-Solution-Vapor. This is also a univariant system, but since the solution phase has a variable composition there are three variables concerned and graphical representation of it calls for a triaxial diagram. Such equilibria are usually measured in open vessels under atmospheric conditions, for as noted in Chapter II, the pressure of air is an additional component, and the slight variations in barometric pressure, have only negligible effects upon the solubility of salts, and upon the partial pressure of the water vapor in equilibrium with

such solutions. For most purposes therefore it is sufficient to represent such equilibria on a temperature-composition diagram in which composition represents either concentration of the liquid phase or that of a mixture of solid phases. Solutions which are saturated at atmospheric conditions with respect to two solid hydrates, or to one hydrate and anhydrous salt, are clearly invariant and must be represented by a definite point on the composition-temperature diagram. Such a point marks the temperature at which the solubilities of the two salts are identical. The vapor pressure associated with the transformation of one solid to the other must equal that of the solution. If an attempt is made to change these conditions by adding or removing heat or by increasing or decreasing the vapor pressure due to water the relative amounts of certain of the phases present must change, but there will be no permanent change in pressure, temperature or concentration as long as all four phases are present. Since the form of a solubility curve depends in part upon the change in heat content, and in part upon the change in volume, accompanying the process of solution and since it is not probable that any two solids should give identical values for the relations existing between these constants, the entire solubility curve must be made up of as many separable parts as there are solid phases concerned. This fact was first recognized by Kopp [16] as a result of the data obtained by Gay Lussac for the solubility of sodium sulfate.

The points at which these separate parts intersect are invariant; they represent points on the solubility curve at which one solid may change into another at equilibrium. These facts are illustrated by Figure 10 which represents the data obtained by Wells and McAdam [17] for the solubility of sodium carbonate. The three parts of the curve, namely AB, BC and CD, represent the solubilities of the solids $Na_2CO_3.10H_2O$, $Na_2CO_3.7H_2O$ and $Na_2CO_3.H_2O$. Still another part representing the solubility of the anhydrous salt must be possible but not within the range of temperature here considered. The AB and BC curves show increasing solubility with increasing temperature, whereas CD shows decreasing solubility with increasing temperature. It will be

[16] See Meyerhoffer, *Z. physik. Chem., 42,* 501 (1903) and *J. Phys. Chem., 8,* 571 (1904).
[17] Wells and McAdam, *J. Am. Chem. Soc., 29,* 724 (1907).

noted also that all three parts of the curve have been followed experimentally beyond the points B and C, indicating the existence of metastable systems. In every case the dotted portions of the curves indicate a solubility greater than that of some one of the other solid phases at the same temperature, and therefore a condition of supersaturation. Such a condition forms a reliable test of metastability in systems of this kind.

Transition Points. The changes which take place at the points B and C of Figure 10 are more complex than those heretofore designated as "inversion points." In the former there is an actual

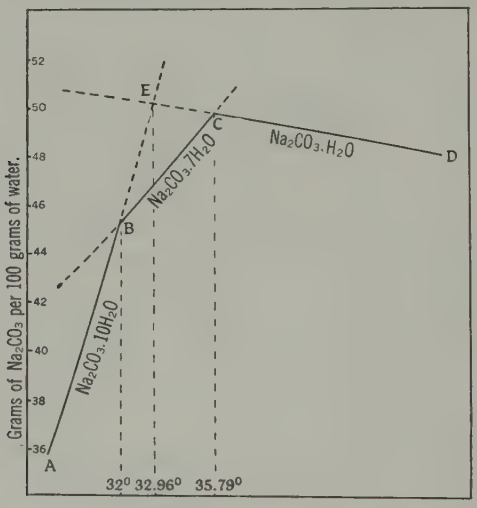

FIG. 10.—Solubility curve for the system water-sodium carbonate.

change in the chemical composition of the solid concerned and an additional product, namely a saturated solution, is also formed; in the latter neither of these changes occurs. Although the terms inversion point and transition point are used interchangeably the distinction is a fundamental one. The point E is also a true transition point although the solid phases concerned are both metastable.

Since all of these points represent invariant systems they also represent intersections on the pressure-temperature-concentration diagram of four curves, each of which represents a univariant system. In every case two of these are solubility curves; for the point B they are AB and BC. A third is a vapor pressure

curve which starts at the transition point in question and ends either at the absolute zero or at its point of intersection with one of the other vapor pressure curves. The fourth expresses the effect of pressure upon systems composed of two solids and a liquid. Since there is no vapor phase present the change in volume resulting from a given increase in pressure is relatively small and the disappearance of any of the phases concerned which might result from a change in pressure, can be prevented by relatively slight changes in either the temperature or the composition of the solution. Hence all three of these curves can be represented with a fair degree of accuracy by straight lines parallel to the pressure axis.

Since no difficulty is experienced in following the solubility curves for the deca- and hepta-hydrates of this salt beyond the stable limit of these solids the transition points B and C can be determined with a high degree of accuracy by finding the points at which these curves intersect. The hydrates of certain salts are found to respond to temperature changes more rapidly than those of sodium carbonate, and in such cases transition temperatures can be determined with a high degree of accuracy by heating some of the solid hydrate at a uniform rate of temperature increase until the thermometer in contact with it ceases to rise temporarily. This procedure simply follows up the vapor pressure curve for the two solids until a liquid phase becomes possible at which point a large amount of heat is absorbed owing to the formation of a liquid and a new solid phase. Many such systems have been found, and the transition temperatures represented have been ascertained with a high degree of accuracy by Richards,[18] who advocates their use in the standardization of thermometers.

Congruent Points. The solubility curves of certain hydrates assume a very different form from those already described. The hydrates of ferric chloride, which were investigated by Roozeboom,[19] illustrate the second type remarkably well. As shown in Figure 11 the curves for all the four hydrates, namely $FeCl_3.6H_2O$, $FeCl_3.7/2H_2O$, $FeCl_3.5/2H_2O$ and $FeCl_3.2H_2O$, are continuous but show clearly defined maxima at the points C, E, G and I. A simple calculation will show that in every case

[18] Richards, *J. Am. Chem. Soc., 40,* 90 (1918).
[19] Roozeboom, *Z. physik. Chemie, 10,* 477-508 (1892).

the composition of the solution at the maximum is identical with that of the solid hydrate with which this solution is in equilibrium. If any one of these solutions were evaporated at this temperature the solid phase would increase at the expense of the liquid phase but the latter would not experience any change in composition. These points have been designated as "indifferent points." No unusual difficulties are presented in their consideration if, in accordance with the proposal of Lorentz and

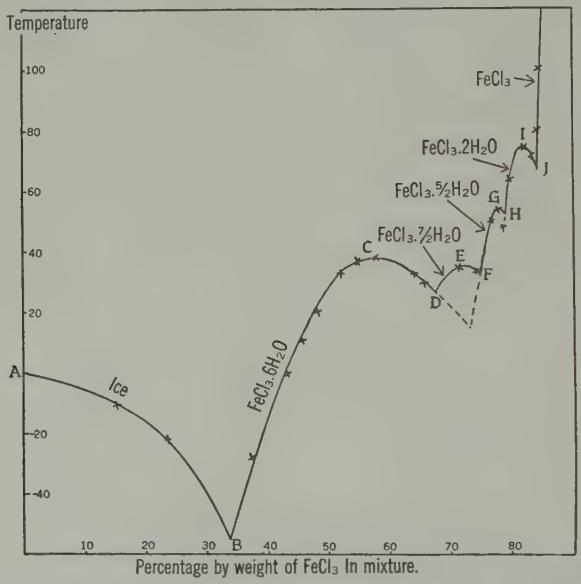

FIG. 11.—Solubility curve for the system water-ferric chloride.

Stortenbecker,[20] we regard them as the melting points of the pure hydrates, and assume that the two portions of the solubility curve, which become continuous at this point, are freezing-point curves, one representing the change in freezing point due to an excess of water and the other that due to an excess of salt or both due to an excess of a higher and a lower hydrate respectively. The melting of such compounds is associated with more or less dissociation into salt and water and a certain amount of ionization, both of which tend to reduce the melting point of the salt below the value it would have if the liquid and solid

[20] Stortenbecker, *Z. physik. Chemie, 10,* 183 (1892).

phases contained the same kinds of molecules in the same proportions. The form of this curve must approach as a limit that of two arcs which intersect at the melting point to form a distinct cusp. The extent to which the actual curves depart from this limiting form measures the extent to which the hydrate is dissociated. If the dissociation of the hydrate is small the addition of a small quantity of either water or ferric chloride will cause a much greater reduction in the apparent melting point than if a large amount of water and salt, resulting from dissociation of the hydrate, is already present. This is a necessary consequence of the mass law. A further extension of the same idea of Lorentz and Stortenbecker is to consider each of the hydrates, which has a definite melting point, as a separate component of that portion of the salt-water system in which it occurs as a solid phase.

If, on the other hand, the entire curve which represents saturation as to a certain hydrate is regarded as continuous then it is characterized by the peculiarity that the same solid is in equilibrium at the same temperature with two solutions which differ as to concentration and vapor pressure. This is due to the fact that there happen to be two sets of concentration and temperature conditions which satisfy all the mathematical equations demanded by the equilibria concerned. The case is analogous to the form of the solubility curve of certain anhydrous salts like potassium nitrate discussed in Chapter II.

A further peculiarity of the systems represented by such curves is shown by the consideration of the vapor pressures concerned. The vapor pressures must show maximum values at points representing solutions containing somewhat more water than the solid hydrate. The pressure of solutions corresponding to points on the BC curve must increase from B owing to the fact that this pressure is increased to a greater extent by the effect of increasing temperature than it is decreased by the effect of increasing concentration of the salt, but as the point C is approached and the temperature begins to fall the vapor pressure must pass through a maximum, which must be somewhat to the left of the point C. From this point the pressure must fall at first slowly and then more rapidly to a minimum at D. The vapor pressure measurements needed to confirm these statements are not available, but similar measurements for the salt $CaCl_2.6H_2O$ were

made by Roozeboom [21] and found to agree with the theoretical predictions.

The points at which the solubility curves of this type intersect, such as D, F, H and J of Figure 11, have all of the properties of true eutectic points. The diagram also shows that certain of these curves, notably those for the six- and five-halves hydrates have been followed far beyond their normal limits, even to the point at which they intersect, with the consequent formation of a metastable eutectic point. All eutectic points as well as all the points on solubility curves at which a true maximum is attained show no change in composition when they are evaporated. In all such cases the composition of the liquid is such that it can be prepared by the use of the solid or solids with which it is in equilibrium in the proper proportions. Such solutions were first designated by Meyerhoffer [22] "congruent solutions" and the points on the diagram representing them may be conveniently designated congruent points.

Solubility Curves and Heats of Solution. The effect of varying temperature upon the solubility of a salt can be predicted qualitatively from the theory of Le Chatelier and quantitatively from the freezing-point equation discussed in the preceding chapter, namely,

$$\frac{d \ln N}{dT} = \frac{\Delta H}{RT^2}$$

in which N is the molal concentration of the dissolved salt, and ΔH is the heat absorbed when one mole of the solid dissolves in a large amount of the nearly saturated solution. Actually but little use can be made of this equation at present as applied to soluble salts since most of the heats of solution which have been determined represent the heat change resulting from the addition of the salt to a large amount of water.

Solubility curves which exhibit inversion points must show abrupt changes for ΔH at these points. Those curves which show indifferent points appear to require a change in the sign of the heat effect at these points, for although the solid phase does not change, its solubility appears to increase with increasing temperature for that portion of the curve which is at the left of the indifferent point but decrease with increasing temperature

[21] Roozeboom, *Z. physik. Chemie, 10,* 471 (1891).
[22] Meyerhoffer, *Ber. Akad. d. Wissenschaft, Wien.,* p. 849 (1895).

for the portion to the right of this point. As shown by Roozeboom [23] however this is not true because of the fact that although the solid contains less water than the solution at the left of the indifferent point it contains more than the solution to the right of it. Hence, while increasing solubility of the solid actually increases the concentration of the dissolved salt, up to the concentration corresponding to the indifferent point, decreasing solubility increases this concentration beyond this point. The value of ΔH for the solid $FeCl_3.6H_2O$ should, according to the data of Figure 11 show a large negative value beyond B, which decreases as C is approached and attains a zero value at that point, but it should also show an increasing negative value between C and D. Roozeboom (*l.c.*) actually found positive values for the heats of solution of the six-, the seven-halves and the five-halves hydrates when dissolved in large amounts of water but negative values when dissolved in solutions containing somewhat more water than the saturated solutions contained.

Effects Resulting from Hydrolysis. In the preceding sections it has been assumed that the water present acts as a solvent only. Certain salts undergo hydrolysis but this does not demand any change in the treatment of systems containing them provided the products of hydrolysis remain dissolved. Since the reaction necessarily yields equivalent amounts of acid and base the solution may still be expressed in terms of the two components, salt and water. This is not true of such salts as $BiCl_3$., $Pb(C_2H_3O_2)_2$ and Na_2WO_4, which form insoluble basic or acidic compounds whose composition, as well as that of the associated liquid phase cannot be expressed in terms of water and a salt. Such systems are three- rather than two-component systems and require different treatment than that outlined in this chapter.

The System Zinc Chloride-Water. The complete composition temperature diagram for a salt-water system may include, in addition to fusion curves for water and anhydrous salt, one or more of the two types of solubility curves represented by hydrated salts. The system zinc chloride-water, which has been carefully investigated by Mylius and R. Dietz,[24] is here represented in Figure 12, showing both kinds of curves. The ice curve AB extends over more than one half the entire range of concentra-

[23] Roozeboom, *Z. physik. Chem., 10,* 500 (1892).
[24] Mylius and R. Dietz, *Z. anorg. Chem., 44,* 209-220 (1903).

tions owing to the very great solubility of the salt even at low temperatures. The curves BC, CD, EF and FG represent solubility curves of the first type and indicate saturation with respect to the tetra-, tri-, the three-halves and the mono-hydrates, although the trihydrate attains a solubility which is but slightly less than its own composition. The five-halves hydrate shows a clearly defined maximum but the slope on either side of the maximum indicates that it is decomposed to a large degree at the melting point. The curve for the anhydrous salt has not been followed

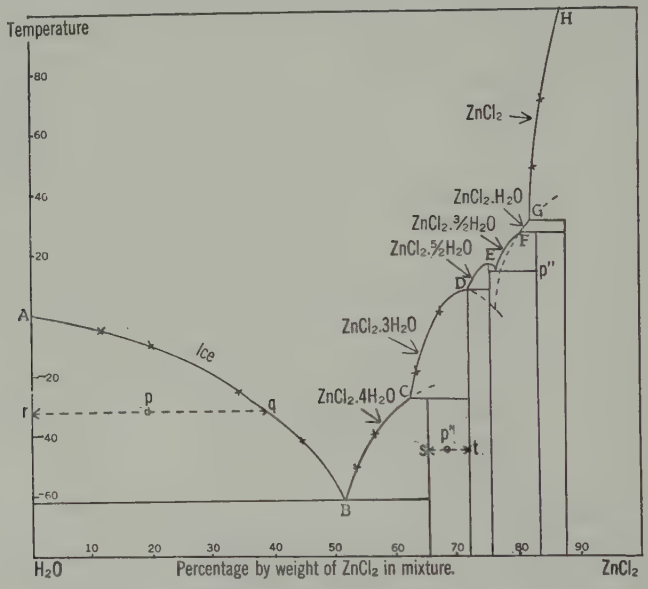

Fig. 12.—Solubility curve for the system water-zinc chloride.

beyond 130° but it is probable that it extends without a break to the melting point which is 262°. Of the invariant points which separate these curves, B and E are clearly eutectic points but C, D, F and G are transition points. The dotted portions of certain of these curves show that their solubility can be followed into the metastable range of values for some distance, and that certain curves of the first type can then be considered curves of the second type if their metastable portion is included.

These investigators report some remarkable instances of supersaturation in this system. A solution containing 83.5 per cent of

$ZnCl_2$ when saturated at 68° could be cooled to zero without crystallization. Such solutions were very viscous and became glassy at — 70°. They probably represent a supercooled liquid.

The Use of Composition-Temperature Diagrams. The composition and relative amounts of the phases present in any mixture of water and a salt can be ascertained by the use of the composition-temperature diagram which represents the system. Composition here represents the ratio in grams or moles between the salt and the total amount of salt and water in the mixture, which may consist of one or more phases. However, since the actual weight of water in the limited amount of vapor phase usually assumed to be present is negligible it can be assumed to be the ratio of salt and water in the mixture of solid and liquid phases present. The complete composition-temperature diagram consists of an area included between the two composition axes, which is subdivided into a number of smaller areas each of which represents the limiting values of the temperatures and compositions within which a certain two- or three-phase system has a stable range of existence. Figure 12 represents such a diagram. The area above the composite solubility curve, that is above the broken line ABCDEFGH represents the system water vapor and a solution which is unsaturated with respect to any solid. Immediately below each of the constituent curves is a field, each one of which represents a system composed of water vapor, a saturated solution of varying composition, and a solid with which this solution is saturated. The limits of these fields on the composition axis are fixed by a series of vertical lines, which correspond to the composition of the particular solid represented. On the temperature axis they are limited by the solubility curve and a horizontal line which passes through either a eutectic point or a transition point. Immediately below this set of fields is another set of six fields each of which represents systems composed of water vapor and two solids. The composition of the solid or liquid phases of systems represented by points below the solubility curve is found by drawing a horizontal line through the point in question until it intersects lines limiting the field in which the point is found. The point p for instance represents vapor, ice and a solution of the composition q because the horizontal line intersects the water axis and the solubility curve at q. It will be noted that all points within this

field have the same significance from the point of view of the phase rule as points in the AB line. Similarly the point p' represents vapor, solid $ZnCl_2.4H_2O$ and solid $ZnCl_2.\frac{5}{2}H_2O$ because the horizontal line intersects the $ZnCl_2.4H_2O$ axis at s and the $ZnCl_2.\frac{3}{2}H_2O$ axis at t. The point p'' is common to the three fields and represents an invariant system consisting of vapor, solid $ZnCl_2.\frac{5}{2}H_2O$, $ZnCl_2.\frac{3}{2}H_2O$ and $ZnCl_2.H_2O$.

It is also possible to calculate the relative amounts of the phases present in such mixtures. The calculation is based upon the obvious fact that a point located on a straight line which joins two other points within such a field must have a composition which is determined by its position with respect to the two points and their composition, and upon the well known lever relation. In the example just cited the concentration of p is 20, that of q is 38.4 and that of r is zero. The percentage of saturated solution in the mixture which p represents must be $(20 - 0) \div (38.4 - 0)$ or 52.1 per cent. In a similar manner all of the changes which would result from elimination of water by evaporation or sublimation of a mixture of known composition can be followed both qualitatively and quantitatively by the use of this diagram.

System with Salts Whose Solubility Is Limited. As noted in Chapter II the solubility of certain salts, at the higher range of temperatures, decreases with increasing temperature thus causing a break in the continuity of the curve connecting the cryohydric point with the triple point. The data obtained by Smits and Wuite [25] for the system sodium sulfate-water, which is represented in Figure 13, illustrates such a system. It will be noted that the solubility of the solid $Na_2SO_4.10H_2O$ increases with the temperature up to the transition point at B, at which point the rhombic modification of the anhydrous salt appears. The solubility of the latter decreases slightly at first, reaches a minimum value at D, and again increases to a second inversion point at E, at which the monoclinic form appears at a pressure of 27.5 atmospheres. The solubility of this solid decreases rapidly with increasing temperature and at the temperature of 365° and a very small concentration of the dissolved salt, shows critical phenomena, that is the properties of the liquid and vapor phases become identical. This point must represent the intersection of

[25] Smits and Wuite, *Proc. Amsterdam Akad., 12,* 245 (1909).

the solubility curve with the critical curve. It is represented by the point F, but has been shifted to the left somewhat in order to make it clear that it does not correspond with the water axis.

The area which represents the system liquid and vapor on this diagram occupies a closed field limited on one side by the water axis. The complete diagram should, in accordance with the statements of page 43, include a second area representing liquid and

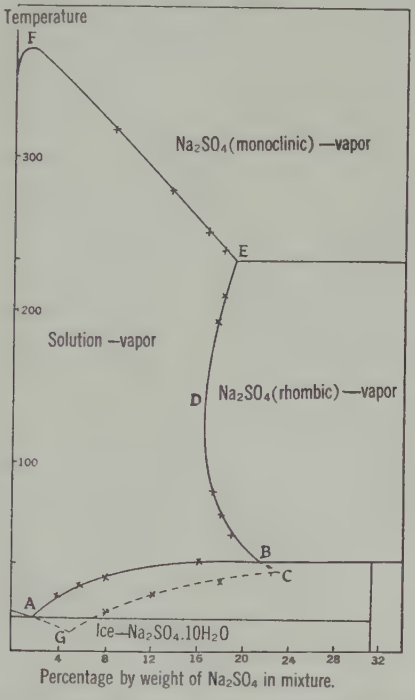

FIG. 13.—Complete solubility curve for the system water-sodium sulfate.

vapor limited on one side by the sodium sulfate axis, and by a second solubility curve, which also intersects the critical curve. Aside from the critical phenomena the diagram is of especial interest on account of the appearance of a heptahydrate, which is metastable at all temperatures but whose solubility curve can be followed over a large temperature range.

Supersolubility Curves. It was suggested by Ostwald,[26] as a result of qualitative experiments on the process of crystalliza-

[26] Ostwald, *Z. physik. Chem.*, *22*, 302 (1897).

tion, that solutions may contain two degrees of supersaturation, a metastable range within which inoculation of the solution with crystals of appreciable size causes a slow growth upon the added crystals, and a labile range within which crystal nuclei are formed spontaneously, either with or without mechanical agitation only. The actual position of a curve on the concentration-temperature diagram, which separates these fields was determined by Meyer and Isaacs [27] for a number of inorganic salts, by Hartley and

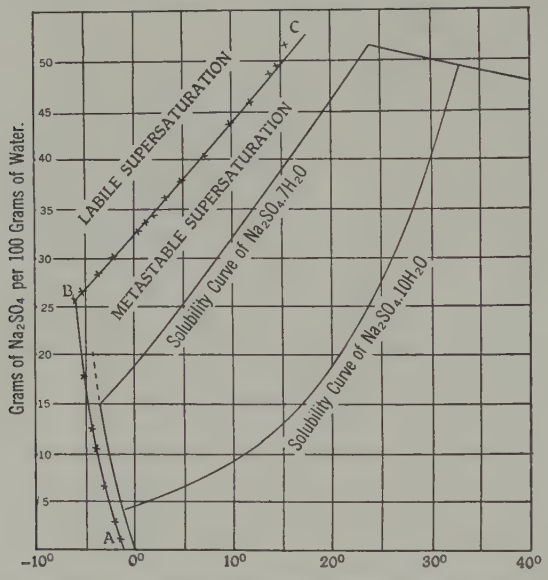

FIG. 14.—Solubility and super-solubility curves for the system water-sodium sulfate.

Thomas [28] for a number of organic compounds and by Hartley, Jones and Hutchinson,[29] who studied the system Na_2SO_4-H_2O with great care. Some of their results are represented in Figure 14 which shows a clearly defined supersaturation curve for ice along AB and for $Na_2SO_4.7H_2O$ along BC, both roughly parallel to the normal solubility curves. They were not able to locate a corresponding curve for Na_2SO_4 from 55° to 95°. Although acceptance of this proposal of Ostwald has been very limited the

[27] Meyer and Isaacs, *J. Chem. Soc., 89,* 427 (1906).
[28] Hartley and Thomas, *J. Chem. Soc., 89,* 1030 (1906).
[29] Hartley, Jones and Hutchinson, *J. Chem. Soc., 93,* 825 (1908).

theoretical explanation offered by Hartley and Thomas (*l.c.*) seems satisfactory. It is based upon the well established fact [30] that, owing to surface tension phenomena, the solubility of a crystal increases as its size decreases and therefore that metastable supersaturation represents supersaturation with respect to crystals of easily recognizable dimensions only.

[30] See Ostwald, *Z. physik. Chem., 34,* 495 (1900) and Hulett, *Z. physik. Chem., 37,* 385 (1901).

Chapter IV.

Systems Composed of Water and Two Electrolytes Which Yield a Common Ion but do not Form Solid Solutions.

The Variables Concerned. Systems composed of water and two electrolytes, which yield a common anion or cation, are three-component systems. Water and the two electrolytes are usually chosen as components but water and the two ions not common to the two electrolytes may be used with equal advantages. With very few exceptions, such as that furnished by the halogen acids, the vapor pressures of the electrolytes at the temperature usually considered are negligible and the vapor phase consists of water vapor only. The composition of the liquid phase can be varied as to two concentrations. The solid phases possible include, in addition to the simple salts and their hydrates, one or more double salts and one or more series of solid solutions both of which may exist in different degrees of hydration. Since the liquid phase may contain variable proportions of all three components its composition, in addition to temperature and pressure, fixes the nature of the entire system.

Of the four variables total pressure is usually disregarded because most experimental work is carried on under atmospheric conditions and the equilibria concerned are not affected by easily measurable amounts unless the pressure variations amount to several atmospheres. The two concentrations may be expressed by a great variety of methods. The ratios of either of the three components to a standard volume of the liquid phase is not advisable owing to the effect of temperature upon the standard volume. Usually the amounts of the two salt components are compared with a standard weight of the liquid phase or with a standard weight of water. It should also be noted that the composition of the entire system can be expressed in terms of the

ratios between the weights of the component salts and the total amount of mixture included in the system. Further, since the weight of the vapor phase is usually very small as compared with that of the solid and liquid phases, its weight can frequently be disregarded in calculating the composition of the mixture. When this simplification is made use of the system is sometimes designated as a "condensed system." The form of the concentration variables made use of is intimately related to the type of diagram employed to represent the system graphically as will become evident from the sections which follow.

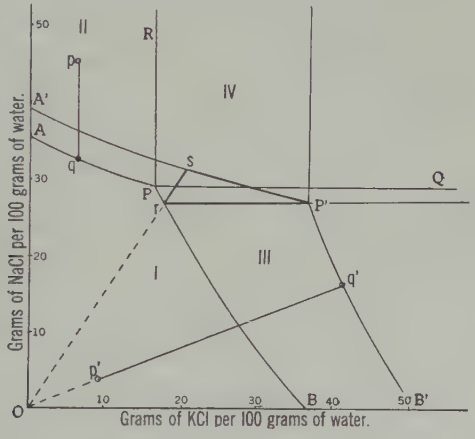

FIG. 15.—The system potassium chloride-sodium chloride-water referred to two axes.

Graphical Representation by Reference to Two Axes. The chlorides of sodium and potassium illustrate a pair of salts which are incapable of forming double salts at any temperature or solid solutions except at temperatures above 450 degrees. If solid KCl be added to a saturated solution of NaCl some of it precipitates as the KCl dissolves. If solid NaCl be added to a saturated solution of KCl some of it precipitates as the NaCl dissolves. In either experiment a point will finally be reached at which the solution becomes saturated as to both salts. If the concentrations of the two salts are expressed in terms of grams per 100 grams of water the system[1] can be satisfactorily represented by means of two axes intersecting at 90° as shown in

[1] For numerical data see Precht and Wittigen, *Berichte, 14,* 1670 (1881) and Blasdale, *J. Ind. Eng. Chem., 10,* 344 (1918).

Figure 15. Points on the AP line represent solutions saturated as to NaCl at 25°, and on BP those saturated as to KCl. The area I, limited by OAPB, represents unsaturated solutions; area II, limited by AP and PR drawn parallel to the vertical axis, represents saturated solutions of variable composition and solid NaCl; area III, limited by BP and PQ, represents saturated solutions of variable composition and solid KCl; area IV, between PQ and PR, represents a solution of the composition P associated with varying proportions of solid NaCl and solid KCl. From the point of view of the phase rule all points within the area II have the same significance as points on AP, those within area III as points on PB and those within area IV as the point P.

At 100° the points A, B and P become A′, B′ and P′ and the lines connecting these points represent the solubility curves for this temperature.

The Use of Diagrams in Quantitative Calculations. Every point included within the space occupied by such a diagram as Figure 15 corresponds to a definite proportion of the three components. Many useful calculations can be made by a combination of algebraic and geometric methods based upon such diagrams. For example, a mixture of 7.5 grams of KCl, 45 of NaCl and 100 of water corresponds to the point p and therefore consists of a mixture of NaCl and a saturated solution of unknown composition. Elimination of the NaCl in excess of that required to saturate the solution would correspond to movement of p, parallel to the NaCl axis, to its intersection at q with the AP line. This point corresponds to 7.5 KCl, 32.5 NaCl and 100 H_2O. Hence, p represents a mixture of 12.5 NaCl and 140 grams of saturated solution of the composition given.

Similarly a mixture of 10 KCl, 4 NaCl and 100 H_2O is represented by p' and consists of an unsaturated solution. If such a solution is evaporated the relative proportions of KCl and NaCl must remain constant while the ratio of both to water changes. These changes would correspond to a movement of the point p' away from O. If evaporated at 100° saturation as to KCl will be attained at q' on the B′P′ line. This point corresponds to 41 KCl, 16.4 NaCl, 100 H_2O. If x represents the water lost by 114 grams of the mixture during evaporation then $10 \div (100 - x) = 41 \div 100$ and x must be 75.6 grams. If the evaporation is continued both water and KCl separate, but as the solution remains

saturated with KCl the change in its composition corresponds to movement from q' to P', at which point KCl = 35.16, NaCl = 27.39, H_2O = 100. If x again represents the water lost by 157.4 grams of the mixture then $41 \div (100 - x) = 35.16 \div 100$ and x must equal 26.74. Further, if y represents the KCl which separates then $(41 - y) \div 16.4 = 27.39 \div 100$ and hence $y = 36.51$. If next the temperature is changed to 25° the solution becomes supersaturated as to KCl only, because P' is located in field III of the 25° diagram, and KCl will continue to separate until the composition of the solution is represented by r. If again evaporated at 100° it loses water until it corresponds to the point s and then water and NaCl until it corresponds to P'. The triangle P'rs represents a cyclic process in which by alternately evaporating at 100°, and, after removal of the separated NaCl, cooling at 25° the separation of the two salts may be effected.[2] This pair of salts is somewhat unusual in that the cooling of solutions saturated as to both salts yields a solution saturated as to one only. This peculiarity is the result of the fact that whereas decreasing the temperature greatly decreases the solubility of KCl it has but little effect upon that of NaCl. The lines AP, BP, A'P' and B'P' are all "crystallization paths." The points P and P' are "crystallization end points" because changes in the composition of the liquid phase end here. They are also congruent points because they can be prepared from water and the two solids with which they are in equilibrium.

The Temperature-Composition Diagram Referred to Three Axes. A more comprehensive insight into the effect of varying temperature upon the NaCl-KCl-H_2O system can be obtained by means of a space diagram in which temperature is measured on a third axis which makes an angle of 90° with the other two, but is conventionally represented on a plane surface at an angle of 45° with the other two, as in Figure 16.[3] The points AA', BB' and PP' on such a diagram may be connected to form "polythermal" lines which outline two surfaces, the various points on which represent solutions saturated as to NaCl and KCl respectively. Two other solids appear at temperatures

[2] Details as to the commercial possibilities of this cycle and discussed by Turrentine and Tanner, *J. Ind. Eng. Chem., 16,* 242 (1924).

[3] The additional data needed for this diagram have been taken from several sources. The position of the point Q is conjectural as actual data are lacking.

below zero, namely ice, corresponding to the surface limited by $OA°B°$, and $NaCl.2H_2O$ corresponding to the surface limited by $QP°A°$. Obviously the points P° and Q represent systems composed of three solids in equilibrium with solution and water vapor and are therefore invariant. Although any mixture whose composition is known represents a definite point within the included space of this type of diagram it is not possible to ascertain the composition of mixtures corresponding to such points from the diagram as represented on a plane surface. This limitation

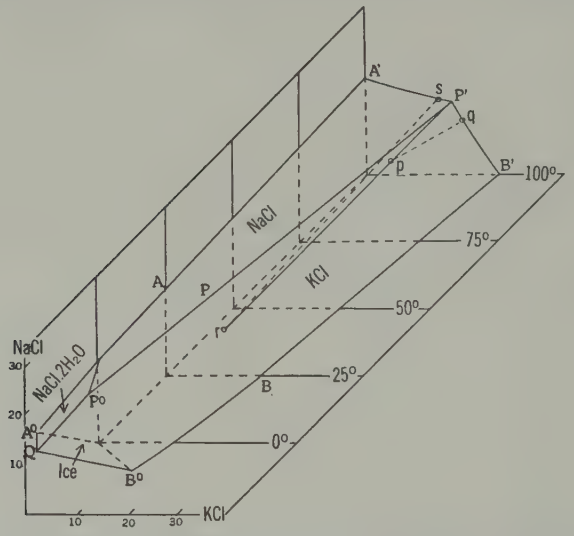

Fig. 16.—The system potassium chloride-sodium chloride-water referred to three axes.

reduces greatly the usefulness of the diagram but the defect may be minimized by projecting the diagram on two horizontal planes. This projection has been made in Figure 17, in which the plane above the heavy horizontal line represents concentration of NaCl and that below it of KCl. The composition of solutions saturated with both NaCl and KCl at any desired temperature may be ascertained by measuring the distance from the point on the heavy line, which represents the desired temperature, to points on the two $P°P'$ lines. The projected diagram can also be used to locate invariant [4] or transition points. If for example two points are

[4] See D'Ans, *Kali, 9,* 151 (1915), and other pages of the same volume.

known on $P^{\circ}P'$ and two on QP° the point of intersection in both planes is easily found and both the temperature and composition of this point can be read directly from the diagram.

Graphical Representation by Use of a Right-angled Isosceles Triangle. If the proportions of the three components in the NaCl-KCl-H_2O system had been expressed in terms of grams per constant amount of the total mixture, the lengths of the two axes of Figure 15 would have been fixed and the entire system would have been included within a right-angled isosceles triangle [5] as shown in Figure 18. It is easily shown that the sum of the distances from any point in the interior of such a triangle to the three sides equals the length of the shorter side provided

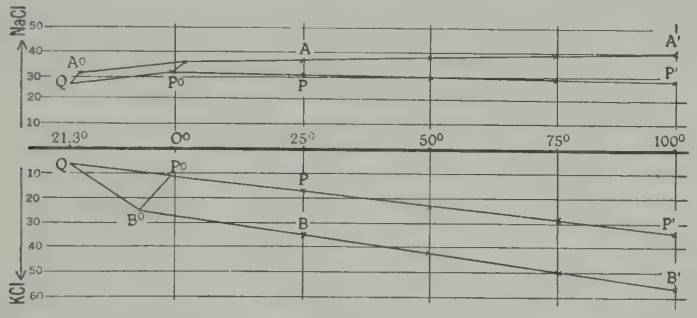

FIG. 17.—Projection of the triaxial diagram for the system potassium chloride-sodium chloride-water.

these distances are measured on lines parallel to the shorter sides. Hence if the shorter sides are given lengths of 100 units the distances measured in this manner correspond to percentages of the three components. The point R of Figure 18 represents pure NaCl and S pure KCl and the line RS every possible mixture of the two salts. The percentage of NaCl corresponding to any point is determined by its distance from OS measured parallel to OR, that of KCl by its distance from OR measured parallel to OS and of H_2O by its distance from RS measured parallel to either OR or OS.

The completed diagram differs essentially from that of Figure 15 in that fields II, III and IV have definite limits. This feature makes it possible to represent any mixture of the three com-

[5] This type of diagram was suggested by Roozeboom, *Z. physik. Chem.*, *12*, 369 (1893), but has not been largely used.

ponents by a point, and to calculate the composition and relative amounts of the phases which any point represents, by the method already used in Chapter III with diagrams representing two-component systems. The diagram may also be used in calculating changes in composition of solutions during evaporation as in the one previously discussed.

Graphical Representation by Use of an Equilateral Triangle. If lines are drawn from any point within an equilateral triangle to its sides in directions parallel to these sides the sum

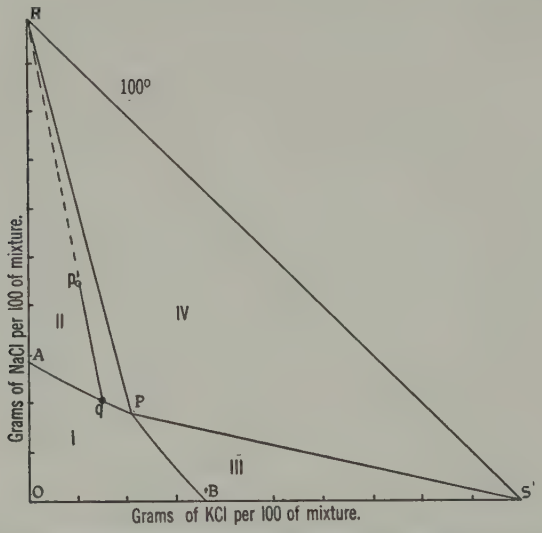

FIG. 18.—Representation of the system potassium chloride-sodium chloride-water by means of an isoceles triangle.

of the distances which these lines represent will equal the length of the sides; if drawn perpendicular to the sides the sum of these distances will equal the altitude of the triangle. Hence in any three component system the apices of the triangle may be assumed to represent 100 per cent and the corresponding opposite sides zero per cent of each of the three components.[6] Its use is shown in Figure 19 which represents the system $(NH_4)_2SO_4$-Na_2SO_4-H_2O at 25° which was investigated by Dawson and

[6] This form of diagram was used by Gibbs, *Trans. Conn. Acad. Sci.*, *3*, 176 (1876), but greatly elaborated by Roozeboom, *Z. physik. Chem.*, *15*, 147 (1894).

Freeth.[7] The solids concerned are $(NH_4)_2SO_4$, which is represented by the lower right apex, $Na_2SO_4.10H_2O$, which is represented by E on the H_2O-Na_2SO_4 side and $(NH_4)_2SO_4.Na_2SO_4.4H_2O$ which is represented by P. The solubility curve ABCD consists of three parts, each part saturated as to one of the three solids. Field I, limited by OABCD, represents unsaturated solutions; field II, limited by E and the solubility curve AB, represents mixtures of $Na_2SO_4.10H_2O$ and saturated solutions of varying composition; field III, limited by P and the solubility

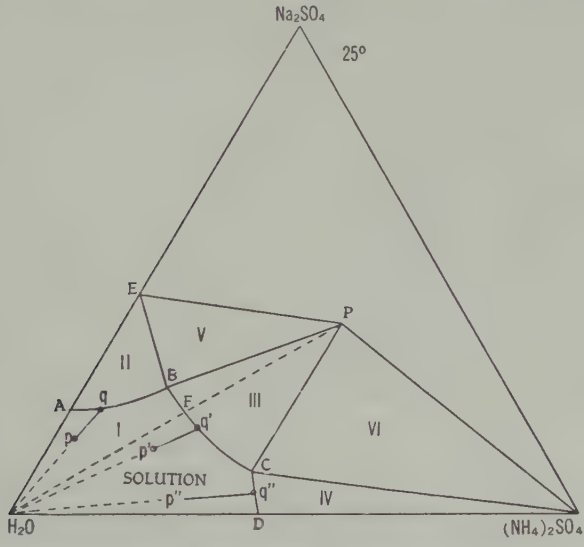

FIG. 19.—Representation of the system ammonium sulfate-sodium sulfate-water by means of an equilateral triangle.

curve BC, represents mixtures of the double salt and saturated solutions of varying composition; field IV, limited by the $(NH_4)_2SO_4$ apex and the solubility curve CD, represents mixtures of $(NH_4)_2SO_4$ and saturated solutions of varying compositions; field V represents mixtures of $Na_2SO_4.10H_2O$, double salt and saturated solution of composition B; and field VI, of $(NH_4)_2SO_4$ double salt and saturated solution of composition C.

The line which joins P with the water apex represents mixtures containing the same proportions of the two-component salts as

[7] Dawson, *J. Chem. Soc., 113,* 679 (1918); Freeth, "Dissertation," Leiden (1924).

the double salt. The fact that it intersects at F that portion of the solubility curve which is saturated as to the double salt proves that F is a congruent point. Since B contains a larger proportion of Na_2SO_4 than the double salt and is saturated with these two solids it is also a congruent point. A similar line of reasoning leads to the conclusion that C is a congruent point.

The changes which result from evaporation at 25° of solutions of known composition are readily followed. If such a solution is represented by *p* it must become saturated with $Na_2SO_4.10H_2O$ at *q*, and this salt will separate until B is reached, after which both $Na_2SO_4.10H_2O$ and double salt will separate without further change in the composition of the liquid phase. If the solution is represented by *p'* the double salt will begin to separate at *q'* and will continue to separate until C is reached after which there is no further change in the composition of the solution. If the solution is represented by *p''* $(NH_4)_2SO_4$ will separate at *q''* and both $(NH_4)_2SO_4$ and double salt at C, after which there is no further change in the composition of the solution. The line which joins the water apex with P divides the field I into two areas and determines whether the crystallization paths move toward the crystallization end points A or B. This in turn depends upon whether the original solution contains Na_2SO_4 or $(NH_4)_2SO_4$ in excess of the ratio in which the salts are present in the double salt.

This type of diagram differs from that of Figure 15 and Figure 18 in that the angle between two of the axes is reduced from 90° to 60°. This procedure necessarily contracts the limits of the different fields, and sometimes yields diagrams in which certain fields are difficult to interpret. Since the equilateral triangle possesses a higher degree of symmetry than the isosceles the composition of the mixture represented by a point within such a triangle can be inferred by mere inspection with greater ease than when an isosceles triangle is used. The chief objection to its use is that a special coördinate paper is needed.

The Concentration-Temperature Diagram Referred to a Prism. If the equilateral triangle used to represent the composition of a three-component system is assumed to lie in a horizontal plane variations in the temperature can be represented upon a series of vertical axes. This procedure forms a regular three-sided prism, each side of which represents one of the three two-

component systems which form the limiting values of the three-component system. It is illustrated in Figure 20, which represents the system NaCl-Na_2HPO_4-H_2O between — 20° and 100°, studied by Okazawa.[8] Only that portion of the diagram which has real significance for the equilibrium in question is shown. There are seven saturation surfaces outlined by curves in space representing solutions saturated as to two, or at the limits of the figure one, solid phases. These surfaces indicate clearly the temperature and concentration limits over which each of the seven solids exist as a stable phase. There are five invariant points

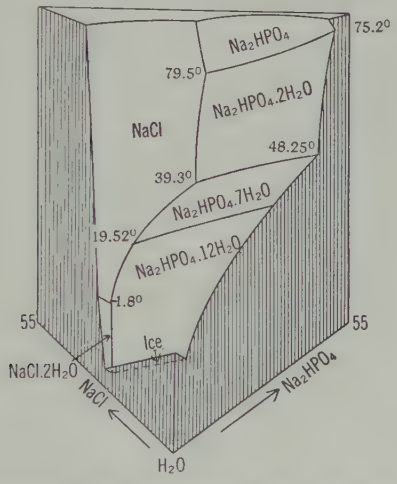

FIG. 20.—The system sodium chloride-disodium hydrogen phosphate-water between — 20° and 100°.

at the intersections of these surfaces in the three-component system and six more in the three two-component systems. As in the concentration-temperature diagram already considered it is not possible to ascertain the composition and temperature of points within the diagram as it has been drawn. It yields however a clear picture of the entire system within the given temperature limits.

Graphical Representation by the Jänecke[9] Method. There is some justification for treating the solvent and the electrolytes associated in such systems differently. Jänecke proposed to rep-

[8] Okazawa, *J. Chem. Soc.*, Tokyo, *41*, 602 (1920).
[9] Jänecke, *Z. anorg. Chem.*, *51*, 132 (1906).

resent them in terms of the amount of water associated with 100 parts of the dissolved anhydrous salts and the percentages of salts in this mixture. The method may be expressed by the formula, x parts of salt A, $100 - x$ parts of salt B, 100 m parts of water in which m is the water associated with one part of salt mixture. The units employed may be either grams, moles or equivalents. Jänecke expresses the relation between these variables graphically by referring the salt percentages to a horizontal line of 100 units length and the amount of water to a vertical axis. It is obvious that by this scheme pure water would be represented by a point at infinite distance from the horizontal base. Jänecke proposes to avoid this defect by expressing distances on the water axis in terms of $100m \div (100 + m)$ rather than by m. If this procedure is adopted pure water is represented by a line 100 units above the horizontal base, and the diagram becomes a closed square or closed rectangle. Although this device yields a diagram which correctly expresses the relations of the different phases to each other it gives a distorted picture of the actual concentrations concerned.

A more important use of Jänecke's scheme is in representing the effect of temperature upon the system. The vertical axis is then used for varying temperature and no attempt made to express the relative amounts of associated water. This is illustrated by Figure 21 which represents the system Na_2SO_4-$MgSO_4$-H_2O between — 10° and 100°. The relative positions of the fields and temperature limits are clearly shown by the figure, and unlike the two concentration-temperature diagrams already described, the temperature and relative amounts of the two salts which correspond to any point on the diagram can be read directly from it. It is necessary for a complete understanding of the system to make use of a numerical table showing the amounts of water associated with some of the important points of the diagram.

The Formation of Double Salts. The factors which determine the formation of double salts were first discussed in detail by Schreinemakers.[10] They are illustrated by means of the temperature-concentration diagram for the system $(NH_4)_2SO_4$-Na_2SO_4-H_2O, which is shown in Figure 22 and represents the

[10] Schreinemakers, *Z. physik. Chem., 11,* 78 (1893).

results obtained by a number of investigators.[11] The field representing solutions saturated with the compound $(NH_4)_2SO_4$. $Na_2SO_4,4H_2O$ is completely closed, being limited by the points P, Q and R. It shows that it is not possible to form this salt from the three components except between — 16° and 59.3°. It can also be shown that this double salt cannot exist in equilibrium with a solution of the pure double salt below 18° nor above 38°, but only between the points A and B. For a wider range

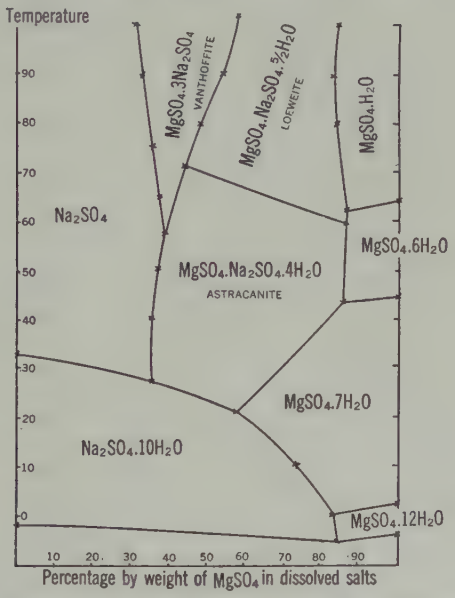

FIG. 21.—The system magnesium sulfate-sodium sulfate-water between — 10° and 100°.

of temperatures it is necessary to have an excess of $(NH_4)_2SO_4$ in the liquid phase. The range of temperatures within which a double salt can exist in equilibrium with a solution of the pure double salt, and the lowest or highest temperature at which it can exist in equilibrium with a solution containing any desired proportion of the component salts is known as a "transition in-

[11] See especially Dawson, *J. Chem. Soc., 113,* 679 (1918); Rivett, *J. Chem. Soc., 121,* 379 (1922); Nishizawa, *J. Chem. Ind.,* Japan, *23,* 25 (1920); Fedotieff and Kolossoff, *Z. anorg. Chem., 130,* 40 (1923); Freeth, "Dissertation," Leiden (1924).

terval." In this example — 16° to 18° and 38° to 59.3° are both transition intervals.

Three different solubility curves meet at each of the points P, Q and R and since three different solids, in addition to liquid and vapor, are also present they represent invariant points. The pressures of water vapor in equilibrium with the three saturated solutions attain identical values at each of these points, and are the same as those of the solid hydrated salts which are also in

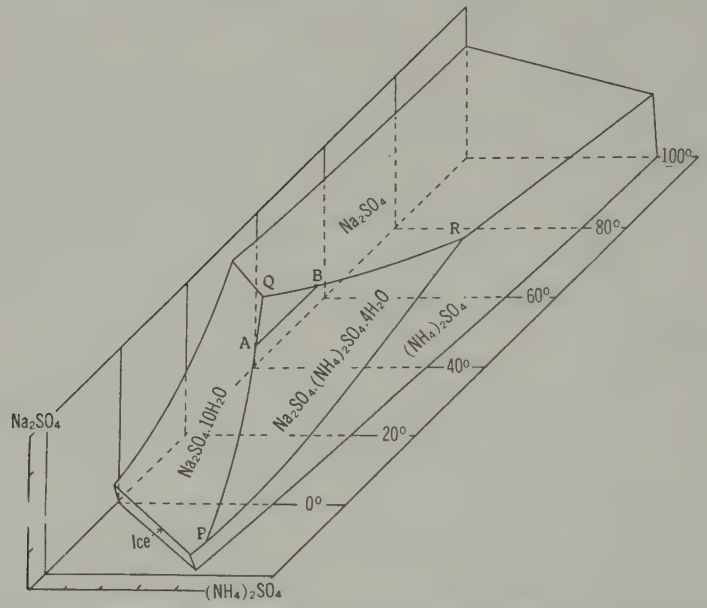

Fig. 22.—The system ammonium sulfate-sodium sulfate-water between — 20° and 100°.

equilibrium at these points. It is possible therefore to ascertain the temperatures to which these points correspond by studying the effect of varying temperature upon the vapor pressure of solutions saturated with the proper solids and also upon the vapor pressures of the solid hydrates.

Systems With Racemic Compounds. Differences in the dextro- and levo-rotatory forms which certain substances assume appear both in the enantiomorphous solids and in the aqueous solutions which they form, and justify considering them independent components rather than allotropic modifications. Certain sub-

stances of this class unite in a 1 : 1 molecular ratio to form racemic compounds which are comparable to double salts. Since the molecular weights and the solubilities of the two forms are identical the corresponding diagrams should, as first suggested by Schreinemakers,[12] be symmetrical with respect to the line which bisects the two axes of reference. Complete data for a system of this kind are lacking but the general features of such a diagram should correspond to those of Figure 23. The curve ABCDE represents the system at T°, at which temperature the racemic compound can exist in contact with solutions whose composition varies from B to D. The A′PE′ curve represents the system at T′°, at which point the temperature limit for the existence of the

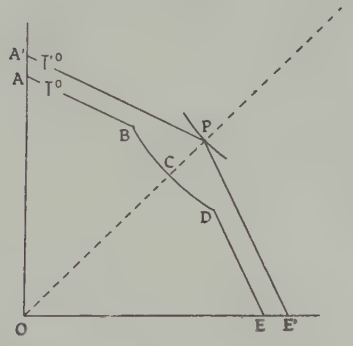

FIG. 23.—Ideal diagram for water and a pair of salts which form a racemic compound.

racemic compound is reached. The point P represents a solution saturated as to both the racemic compound and the two optical antipodes; it is obviously an invariant point. No transition interval is possible in such systems.

Most of the water-soluble racemic substances are themselves double salts. Systems which include racemic compounds of double salts are not three-component systems unless the dextro and levo forms can be used as components. This is only possible when both liquid and solid phases contain the constituent salts in the same proportions as in the double salt, and this condition cannot be complied with unless the temperature of the system is within the transition interval.

[12] Schreinemakers, *Z. physik. Chem., 28,* 495 (1899).

Further Examples of Double Salt Diagrams. Diagrams which include as solid phases a single double salt, whose component salts are not combined in a 1 : 1 ratio, or which differ greatly in solubility, usually show a greater lack of symmetry than those already considered. Those in which several double salts are concerned show a correspondingly larger number of fields and invariant points. Several systems which illustrate these statements are described in the following paragraphs.

A portion of the diagram for the system $MgCl_2$-KCl-H_2O [13]

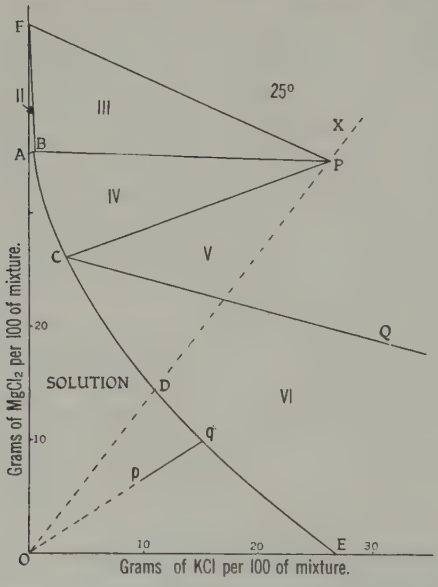

FIG. 24.—The system magnesium chloride-potassium chloride-water at 25°.

when represented by means of an isosceles triangle is shown in Figure 24. It shows much distortion due, for the most part, to the relatively large differences in the solubilities of the component salts; the double salt, which is known as carnallite and is one of the most important constituents of the Stassfurt salt deposits, and has the formula $MgCl_2.KCl.6H_2O$, has no transition interval. This compound corresponds to the position of the point P and the line OP represents all possible mixtures of water and

[13] For data see van't Hoff and Meyerhoffer, *Z. physik. Chem., 27,* 84 (1898) and *30,* 77 (1899); also Lee and Egerton, *J. Chem. Soc., 123,* 714 (1923).

the two salts in molal proportions. This line intersects the solubility curve at D, at which point there is saturation as to KCl. That portion of the curve representing saturation as to carnallite, namely BC, is near the $MgCl_2$ axis. If a solution of composition *p* is evaporated it will become saturated with KCl at *q* and KCl will continue to separate until the solution attains the composition C. If the separated KCl is not removed further evaporation changes it to carnallite, but the composition of the solution does not change because the formation of carnallite requires a larger proportion of KCl than the solution itself contains. After all the solid KCl has been changed to carnallite further evaporation causes the solution to change to B because the elimination of carnallite increases the ratio of $MgCl_2$ to KCl in the residual solution. At B however the proportion of $MgCl_2$ has become so large that saturation with $MgCl_2.6H_2O$ is attained, and a crystallization end-point is reached. If the KCl which separates along EC is removed the separation of carnallite and subsequent changes in the composition of the solution begin to take place at once. Aside from A and B the only congruent point is E.

The point F corresponds to the solid $MgCl_2.6H_2O$ and the points A, F and B define the field II of the diagram, representing varying proportions of the solid $MgCl_2 . 6H_2O$ and saturated solutions whose composition varies from A to B. Similarly field IV, limited by P, B and C represents varying proportions of carnallite and saturated solutions whose composition varies from B to C. Also field VI, limited in part by the points Q, C and E represents varying proportions of KCl and saturated solutions whose composition varies from C to E. Field III, between fields II and IV, represents varying proportions of $MgCl_2.6H_2O$, carnallite and solution of composition B. Field V, between fields IV and VI, represents varying proportions of KCl, carnallite and saturated solution of composition C. All of these facts are in agreement with the phase rule.

The diagram clearly requires that if carnallite be added to water, solid KCl will be the first solid to separate, and a large percentage of the KCl in this mineral can be obtained in pure form by simply adding water and evaporating. Still greater yields can be obtained by working at higher temperatures.[14]

[14] For a discussion of the details of this process see Boeke, *Kali*, *4*, 14 (1910).

A similarly constructed diagram for the system $(NH_4)_2SO_4$-$MgSO_4$-H_2O at 30°, studied by Weston,[15] is shown in Figure 25. It illustrates the formation of a double salt having the formula $(NH_4)_2SO_4.MgSO_4.6H_2O$, whose solubility is small as compared with that of the other solids concerned, namely $(NH_4)_2SO_4$ and $MgSO_4.7H_2O$. Its solubility curve was followed through a wide range of concentrations but not to the point of saturation with either of the other solids. The point P represents the composition of the double salt and the curve BC its solubility although its limits, that is the positions assigned to B and C, are conjectural.

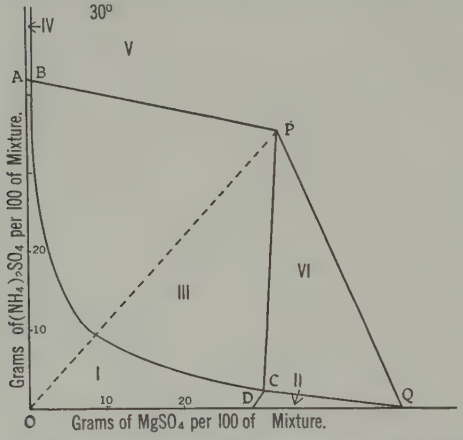

FIG. 25.—The system ammonium sulfate-magnesium sulfate-water at 30°.

The lines AB and CD representing the solubility curves for $(NH_4)_2SO_4$ and $MgSO_4.7H_2O$ are very short.

A similarly constructed diagram for the system K_2SO_4-Na_2SO_4-H_2O [16] is shown in Figure 26. It illustrates the formation of a double salt whose components are not combined in a 1 : 1 molal ratio. The double salt concerned is known as glaserite and is represented approximately by the formula $K_3Na(SO_4)_2$.[17] The

[15] Weston, *J. Chem. Soc., 121,* 1227 (1922).

[16] Meyerhoffer and Saunders, *Z. physik. Chem., 28,* 46 (1899); D'Ans, *Kali, 9,* 163 (1915); Blasdale, *J. Ind. and Eng. Chem., 10,* 346 (1918).

[17] The work of van't Hoff and Barschall, *Sitzber. preuss. Akad. wiss.*, p. 359 (1903), and of Osaka, *Mem. Col. Sci.*, Kyoto Imp. Univ., *1,* 95 (1914), showed that, at least between 15° and 80°, solid $K_3Na(SO_4)_2$ dissolved Na_2SO_4 to a slight extent but not K_2SO_4. The properties of these solid solutions differ but slightly from those of the pure double salt, and these differences have been disregarded in most of the work done on this system.

solubility curve shows saturation as to K_2SO_4 along AB, as to glaserite along BC and as to $Na_2SO_4.10H_2O$ along CD. The line OX represents mixtures of K_2SO_4 and Na_2SO_4 in the molal proportions of 3 : 1 and since it does not intersect BC glaserite is not stable in solutions derived from glaserite and water. The point C is a crystallization end point and A, C and D are the only congruent points.

The field II, limited by AB and a line extending from B through P to the point on the vertical axis corresponding to pure

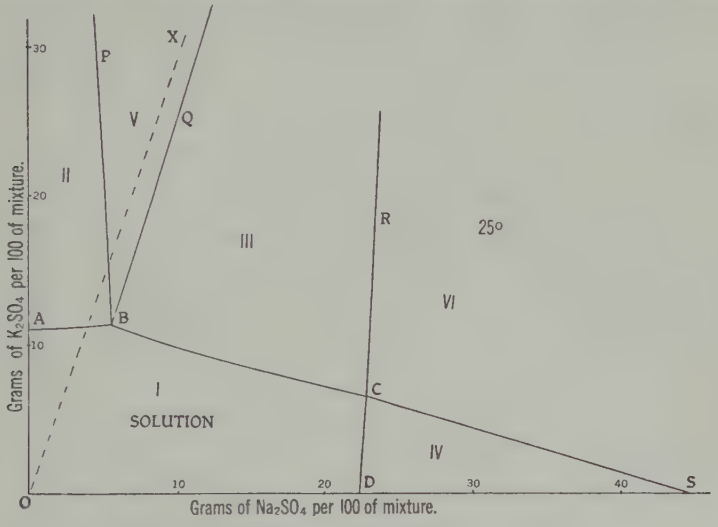

FIG. 26.—The system potassium sulfate-sodium sulfate-water at 25°.

K_2SO_4, represents varying proportions of K_2SO_4 and saturated solutions of varying composition. Field III, limited by BC and lines drawn from B through Q and from C through R to a point on the side of the triangle not shown on the diagram, which represents the composition of glaserite, represents mixtures of glaserite and saturated solutions of varying composition. Field IV, limited by CD and a line joining C and the point S which corresponds to the composition $Na_2SO_4.10H_2O$, represents mixtures of $Na_2SO_4.10H_2O$ and solutions of varying composition. Field V, limited by fields II and III, represents mixtures of K_2SO_4, glaserite and solutions of composition B. Field VI, limited by fields III and IV, represents mixtures of glaserite, $Na_2SO_4.10H_2O$ and solution of composition C.

The system $(NH_4)Cl$-$HgCl_2$-H_2O, studied by Meerburg,[18] is somewhat more complex and has been represented by use of an isosceles triangle in Figure 27. Four different double salts and the component single salts give a total of six solid phases and therefore the solubility curve shows five breaks. The determination of the solid phases in such systems is often troublesome owing to the difficulty of separating the solid in equilibrium with

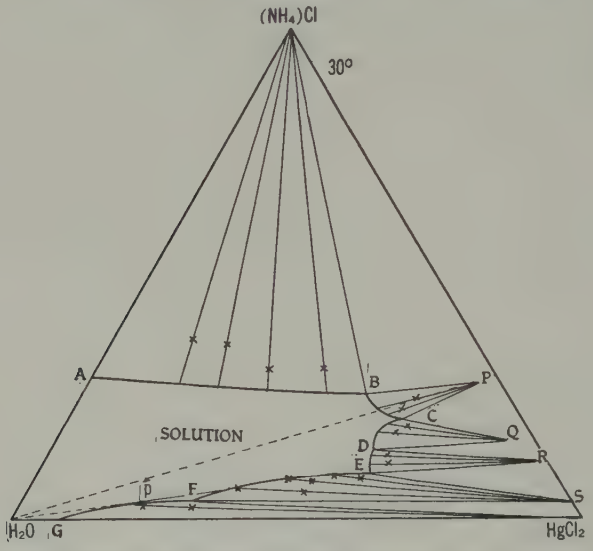

FIG. 27.—The system ammonium chloride-mercuric chloride-water at 30°.

the liquid phase from the adhering mother liquor without changing its composition. Although it was found possible in this investigation to identify the six solid phases concerned additional evidence of the accuracy of the work was obtained by use of the "residue method" of Schreinemakers.[19] It consists in making analyses of some of the saturated solution and of a mixture of some of this solution and the solid with which it is in equilibrium. The composition of the mixture must correspond to a point on the diagram which is located on the straight line connecting the composition of the solid and the saturated solution. If a line is drawn through the two points representing the two analyses it must pass through the point representing the composition of the

[18] Meerburg, *Z. anorg. Chem., 59,* 139 (1908).
[19] Schreinemakers, *Z. physik. Chem., 43,* 307 (1903).

solid. If the directions of a number of such lines are ascertained the point toward which they converge must represent the composition of the pure solid. If the solutions used are not saturated with the same solid, or if saturated with more than one solid, these lines will not converge towards a common point. The diagram shows that four points on the AB portion of the solubility curve were correlated with four points representing mixtures of these solutions and of a solid, which mixtures are represented by crosses. The lines which connect these points all converge towards the $(NH_4)Cl$ apex of the triangle, clearly showing that this part of the solubility curve was saturated with ammonium chloride. Similarly lines drawn through points on the other sections of the solubility curve converge towards P, representing $2(NH_4)Cl.HgCl_2.H_2O$; towards Q, representing $(NH_4)Cl.HgCl_2.H_2O$; towards R, representing $2(NH_4)Cl.3HgCl_2.H_2O$; towards S, representing $2(NH_4)Cl.9HgCl_2$; and towards the $HgCl_2$ apex of the triangle. No large degree of accuracy can be claimed for this process as carried out in this investigation as it is obvious that slight errors in the location of the points representing the solid-liquid mixture must have a large effect upon the angles between the converging tie lines. If the mixtures used had contained larger proportions of solids these differences would not have affected the results to nearly so large a degree. The method is widely and successfully used in investigations of this character.

Only one of the six sections of the solubility curve is intersected by a line joining the point representing the composition of the solid with which that section is saturated and the H_2O apex of the triangle. Hence only one of the four double salts can exist in equilibrium with an aqueous solution of that salt. This is the salt $2(NH_4)Cl.HgCl_2.H_2O$. This point of intersection, the adjacent points B and C and the points A and G are the only congruent points of the system. The points B and C are also crystallization end points. The changes which take place on evaporation of a solution such as *p* involve the separation of $2(NH_4)Cl.9HgCl_2$, conversion of this into $2(NH_4)Cl.3HgCl_2.H_2O$ at E, the separation of more $2(NH_4)Cl.3HgCl_2.H_2O$ and conversion of this into $(NH_4)Cl.HgCl_2.H_2O$ at D, separation of further quantities of $(NH_4)Cl.HgCl_2.H_2O$ until the point C is reached.

Chapter V.

Three Component Systems Derived from Water and Two Electrolytes Which Yield a Common Ion and Form Solid Solutions.

General Features of Solid Solutions. It was recognized very early in the history of modern chemistry that certain pairs of salts were capable of forming solids, which appeared to be homogeneous, although the ratios of the component salts of which these solids were composed did not conform to a simple stoichiometric ratio. Beudant [1] designated them as "mélange chimique" but Wollaston [2] endeavored to show that they represented some form of double salt. The discovery of the Law of Isomorphism by Mitscherlich in 1819 led to the recognition of the fact that certain salts formed solids, whose crystallographic constants were either identical or very similar, and that such salts were able to crystallize together in variable proportions. This established the fact that such salts must be regarded as mixtures rather than compounds and Retgers in 1889 used this property of forming such mixtures as a test of isomorphism and made use of the term "mixed crystal" to designate them. The fact that the composition of such crystals was determined by the temperature at which they were formed was first clearly stated by Roozeboom,[3] who also showed that they should be treated as phases of variable composition. The analogy between the properties of liquid and solid solutions was recognized and discussed at length by van't Hoff,[4] who made use of the term solid solution although the term solid solvent had been used by Boisbaudran [5] as early as 1866. At present the terms solid solution and mixed crystal are used synonomously.

[1] Beudant, *Ann. des Mines, 3,* 239 (1818).
[2] Wollaston, *Ann. of Phil.,* II, 283; *Ann. Chim. Phys.* (2), *7,* 399 (1818).
[3] Roozeboom, *Z. physik. Chem., 8,* 511 (1891).
[4] van't Hoff, *Z. physik. Chem., 5, 323* (1890); *Vorlesungen* I, 49.
[5] Boisbaudran, *Comptes Rendus, 113,* 832 (1891); *142,* 195 (1906).

Although there can be no valid objection to applying the term solid solution to homogeneous mixtures of solids as well as gases and liquids, the mixtures in question are not strictly speaking homogeneous, if the nature of the ultimate units of which such crystals are made up is considered. The term homogeneous as here used is in accord with the definition of Barlow [6] which assumes that "a homogeneous structure is one every part within which, if we regard the structure without boundaries, has corresponding to it an infinitude of other points whose situations in the structure are precisely similar." The character of the structure here defined would seem to demand a slow rate of diffusion of the two components and to present serious difficulties in explaining how such structures originate and how they respond to changes in temperature and concentration of the liquid phase with which they are in equilibrium. The experiments [7] on the rate of diffusion of the components of certain alloys have, however, shown rather surprisingly rapid rates of diffusion at moderately high temperatures.

Solid Solution and X-Ray Analysis. The use of the X-ray has thrown much light upon our knowledge of the nature of solid solutions. A large proportion of the work done has been concerned with solutions of metallic solids but Vegard [8] and also Havighorst, Mack and Blake [9] have reported some work on solid solutions of the halides of ammonium and the alkalies. They found that X-ray photographs, taken by the method of Debye and Hull, gave lines occupying positions intermediate between those occupied by the component salts and concluded that the solid solutions between salts of this series of components resulted from the substitution of atoms of one salt for those of the other in the space lattice, which could be either face-centered or body-centered. The investigators last named found that miscibility was not possible, or that the limit of miscibility was reached at very small concentrations, if the differences in molecular volume were large. These conclusions are in agreement with the results obtained in the study of metallic solid solutions. As to whether the substituted atoms are arranged according to a regular plan or not there are differ-

[6] Barlow, *Mining Magazine, 11,* 119 (1895).
[7] See Bruni and Memighini, *Atta accad. Lincei* (L), *20,* 671 and 972 (1911); Fraenkel and Houben, *Z. anorg. Chem., 116,* 1 (1921).
[8] Vegard, *Z. physik. Chem., 5,* 17 (1921).
[9] Havighorst, Mack and Blake, *J. Am. Chem. Soc., 47,* 31 (1925).

ences of opinion. Vegard thought they were not because the x-ray photographs did not show additional lines. Tamman found, as the result of a long series of studies on the action of certain liquids upon solid solutions, whose components differed greatly as to ease of attack by these reagents, that a minimum degree of attackability was reached at a number of fairly well-defined concentrations of the component solids and concluded that these components were regularly spaced in the lattice.

It should be noted also that although solid mixtures made up of solids of simple constitution, such as the metals and simple halide salts, consist of single atoms arranged according to a simple plan, it has been shown by Bragg [10] and others that certain nonpolar substances yield solids in which the space lattice is made up of groups of atoms or molecules. Bragg found that the structural units of crystals of napthalene consisted of two molecules and those of alpha- and beta-naphthol of four molecules.

Classification of Solid Solutions. The formation of one of these solids in a system adds a new solid and a new concentration variable to that system. If the temperature is fixed either pressure or one of the three concentration variables can be varied within certain limits, but if any one of these is fixed the entire system is defined. Equilibrium requires that the fugacities of the two components in the solid equal those of the same components in the liquid. The relations between the concentrations of the two components in the solid and liquid phases, which are in equilibrium, must depend upon the values of the fugacities of the pure components, and the rates at which these values are changed by the presence of varying concentrations of each other in both phases, and by the presence of water in the liquid state. These relations are complex and as a necessary consequence several different types of systems containing such solids are possible. Roozeboom [11] using the analogy to liquid solutions as a guide, showed that five different types are possible. These types depend upon the mutual solubility of the two salt components in the solid phase or phases possible. Type I includes systems in which the miscibility is complete and the concentration of one of the two salts in the liquid phase exceeds that of the same salt in the solid phase for all concentrations. Type II includes systems in which the

[10] Bragg, *J. Chem. Soc., 121,* 2766 (1921).
[11] Roozeboom, *Z. physik. Chem., 8,* 521 (1891).

miscibility is unlimited, but while the concentration of one of the salts in the liquid phase exceeds that of the same salt in the solid phase for a certain range of concentrations it is less for the remaining concentrations. In such systems there must be one specific concentration at which the proportions of the two salts in the liquid and solid phases are identical. Type III includes systems in which the miscibility is complete, but while the concentrations of one of the salts in the liquid phase is less than that of the same salt in the solid phase for a certain range of concentrations it is greater for the remaining concentrations. In this class also there must be a specific concentration at which the proportions of the two salts in the liquid and solid phase are the same. Type IV includes systems in which, owing to incomplete miscibility, there is a discontinuity in the properties of the solid phase and it becomes necessary to assume the presence of two different solid phases. In this class one of the solids contains a smaller concentration of one of the salts in the liquid phase than in the solid phase with which it is in equilibrium, the other a larger proportion of this salt in the liquid than in the solid phase with which it is in equilibrium. Type V also includes systems in which there are two series of solid solutions but the proportions of one of these salts in the liquid phase exceeds that of the same salt in both of the solid phases.

When the liquid phases associated with these five different types of systems are evaporated characteristic differences of behavior arise. These differences will be exhibited by brief descriptions of systems of each of the five classes.

Solid Solution of Type I. This type is illustrated by the system [12] KH_2AsO_4-KH_2PO_4-H_2O. It is represented by Figure 28, in which the percentage of KH_2AsO_4 in the mixture of KH_2AsO_4 and KH_2PO_4 in the saturated solution is plotted on a vertical axis, and that of the same salt in the solid with which this solution is in equilibrium on the horizontal axis. Since both axes are given a length of 100 units the completed diagram forms a closed square, and the curve ABCDE represents the relation between the composition of the liquid and solid phases. If the percentages of KH_2AsO_4 in the liquid and solid phases were the same for all concentrations this relation would be represented by

[12] Muthmann and Kuntze, *Z. Kryst.*, *23*, 371 (1894).

the diagonal AE. The experimentally-determined curve is continuous and entirely above the diagonal, indicating that the liquid always contains a larger percentage of KH_2AsO_4 than the solid. The changes which must take place if solutions of the salts are evaporated can be followed both qualitatively and quantitatively by the use of the diagram. If the point *p*, corresponding to a solution in which 38 per cent of the dissolved salts is KH_2AsO_4 and 62 per cent is KH_2PO_4, represents such a solution *q* will represent the system when saturation is attained and the solid

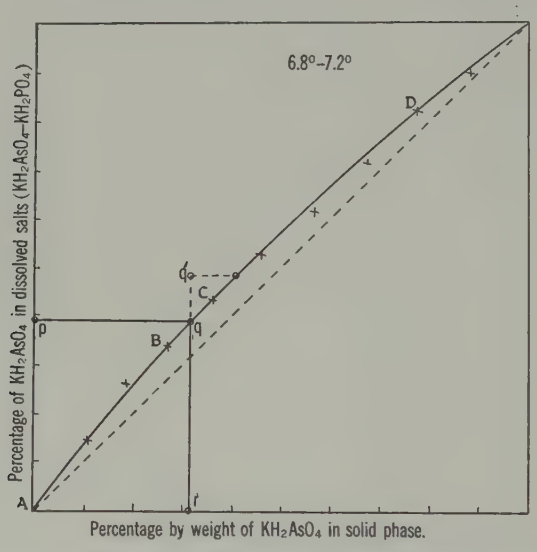

FIG. 28.—The system dihydrogen potassium arsenate-dihydrogen potassium phosphate-water, illustrating solid solutions of type I.

which separates must contain 32 per cent of KH_2AsO_4. If an appreciable quantity of this solid is made to separate the percentage of KH_2AsO_4 in the liquid must be increased because *rq* exceeds *pq*, and *q* would tend to move toward *q'*, but these changes must follow the equilibrium curve and the system therefore changes toward C, not toward B. The evaporation of any solution of these salts will first yield a system on the AE line which will move toward E as evaporation progresses.

It should be noted however that a certain amount of readjustment must take place in the composition of the solid which separates during the earlier stages of the evaporation, and the

liquid with which it is no longer in equilibrium. Such an adjustment demands diffusion from the surface to the interior of the solid concerned, which is necessarily a slow and incomplete process. The adjustment however must materially reduce the changes in the composition of both phases which take place before the liquid phase is used up. These considerations also suggest some of the experimental difficulties in determining accurately the form of the equilibrium curve. Unless the solid used for the analysis is made to separate from a very large amount of solution or

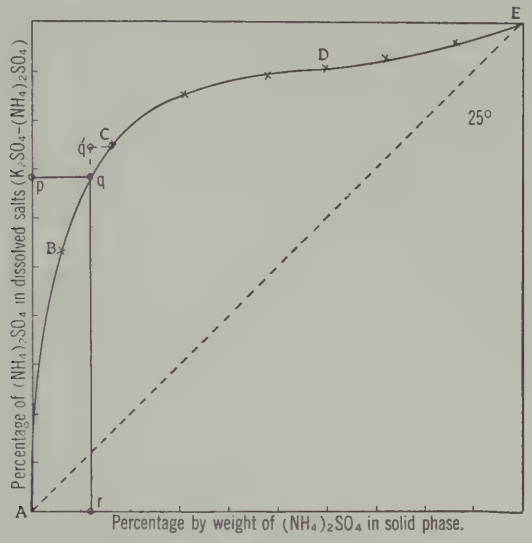

FIG. 29.—The system ammonium sulfate-potassium sulfate-water, illustrating solid solutions of type I.

unless kept in contact with the solution for a long time, during which further evaporation is prevented, large errors in determining this relation may result.

If either of the two methods previously used to represent three-component systems had been employed to represent this one the resulting solubility curve would have appeared as a continuous curve connecting a point on the KH_2AsO_4 axis with one on the KH_4PO_4 axis. Either type of diagram clearly indicates the striking feature of the system, namely, the absence of either a congruent point or of a definite crystallization end point.

A second illustration of systems of this type is furnished by

$(NH_4)_2SO_4$-K_2SO_4-H_2O at 25°, which was studied by Weston,[13] and is represented by Figure 29. The essential difference between it and the system just described is the much greater difference between the composition of the solid and liquid phases which are in equilibrium. In this case the evaporation of any solution of these salts must result in changes corresponding to a movement of the point representing the original system along AE toward E. In this case it is possible to effect large changes in

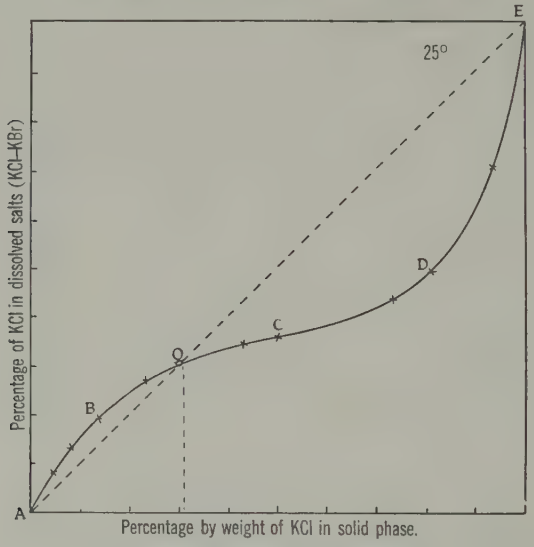

FIG. 30.—The system potassium chloride-potassium bromide-water, illustrating mixed crystals of type II.

the composition of a solid mixture of the component salts by a fractional crystallization.

Further illustrations are furnished by the system K_2CrO_4-K_2SO_4-H_2O at 25°, investigated by Amadori and Pampini.[14] In all of these cases the fugacity of the water in the saturated solution decreases continuously as the solid varies in composition from that of one pure salt to that of the other. In general evaporation of solutions of such salts will cause them to change in composition toward the point representing solutions saturated with a pure

[13] Weston, *J. Chem. Soc., 121,* 1229 (1922).
[14] Amadori and Pampini, *Atta. Accad. Linc.* (V), *21,* I, 667 (1911).

component, namely with that component in whose saturated solution the water has the smaller fugacity.

Solid Solutions of Type II. The system KBr-KCl-H_2O, investigated by Amadori and Pampini,[15] illustrates this type. It is represented by Figure 30. In this diagram the equilibrium curve ABCDE intersects the diagonal at O, corresponding to 31 per cent of KCl, at which point the liquid and solid phases contain the same proportions of the component salts. Between A and O the equilibrium curve is above the diagonal and the changes resulting from the evaporation of solutions containing less than 31 per cent of KCl and more than 69 of KBr correspond to movement of some point on the AO curve toward O. Beyond O the equilibrium curve is below the diagonal and the evaporation of solutions containing more than 31 per cent of KCl must cause a decrease in the percentage of KCl in these solutions, and movement of the point representing them toward O. This point is therefore both a congruent point and a crystallization end point. It also represents a point at which the fugacity is at a minimum. The representation of this system by means of two rectangular axes, one representing KCl and the other KBr per constant amount of water or of saturated solution would make it impossible to distinguish it from systems of Type I. The solubility curve is continuous and would not show any distinguishing feature at the congruent point.

Solid Solutions of Type III. This type is illustrated by the system $PbBr_2$-$PbCl_2$-H_2O, studied by Meyer,[16] and represented by Figure 31. In this diagram also the equilibrium curve intersects the diagonal but the ABCD portion of it is below and the remainder, as far as it can be followed, above the diagonal. It is clear that O is a congruent point, but it is easily shown that it is not a crystallization end point. If a solution of composition *p* is evaporated it attains saturation at *q;* as the solid contains 38 per cent $PbBr_2$ and the liquid only 18 per cent further separation must cause the system to move from *q* towards B. In general any solution containing less than 56 per cent of $PbBr_2$ per 44 of $PbCl_2$ must yield solutions which change on evaporation from O toward A. Similarly it can be shown that solutions containing more than 56 per cent of $PbBr_2$ must change to corre-

[15] Amadori and Pampini, *Atta. Accad. Linc.* (V), *20,* 475 (1911).
[16] G. Meyer, *Rec. Trav. Chim., 42,* 304 (1923).

spond with a movement of points on OE toward E. Hence, although O is a congruent point it is not a crystallization end point. It is also clear that O represents the point at which the fugacity of the water in the saturated solution has a maximum value.

Solid Solutions of Type IV. A very large number of systems belong to this type. The system $(NH_4)Cl$-KCl-H_2O, investigated by Uyeda,[17] has been chosen as an illustration. It is represented by Figure 32 for three different temperatures. It

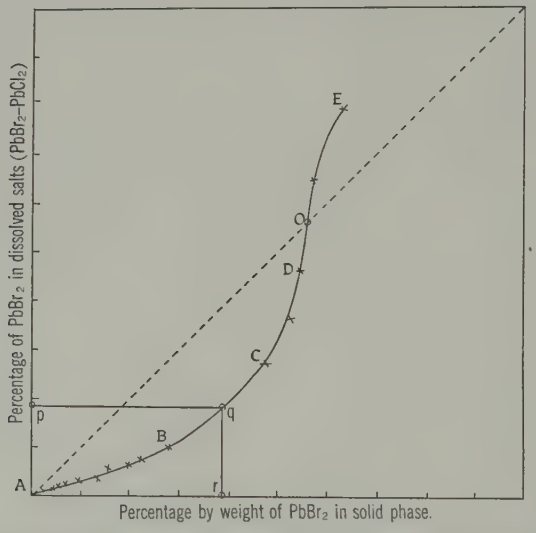

FIG. 31.—The system lead bromide-lead chloride-water, illustrating solid solutions of type III.

will be noted that the equilibrium curves for all three temperatures show a horizontal portion which is intersected by the diagonal. This indicates a constant composition for the liquid phase, which requires the presence of an additional phase, and as we assume only one liquid phase the additional phase must be a solid. It consists of a second solid solution, and the horizontal portion of each of the three graphs corresponds to a break in the continuity of the mixed crystal series, and establishes the limits of their composition. At 25° crystals of Series I can contain from 0 to 21 per cent and of Series II from 87 to 100 per

[17] Uyeda, *Eighth Int. Cong. Appl. Chem.*, *22*, 237 (1912).

cent of $(NH_4)Cl$. Crystals of Series I, containing a maximum amount of $(NH_4)Cl$, and of Series II containing the minimum amount of $(NH_4)Cl$ are called saturated mixed crystals. It is obvious that the only congruent solution possible is the one in equilibrium with both saturated mixed crystals simultaneously. Since the curve representing saturation with crystals of Series I is above the diagonal evaporation of solutions containing less than 21 per cent of $(NH_4)Cl$ must cause such systems to move towards the point B and since the curve representing saturation

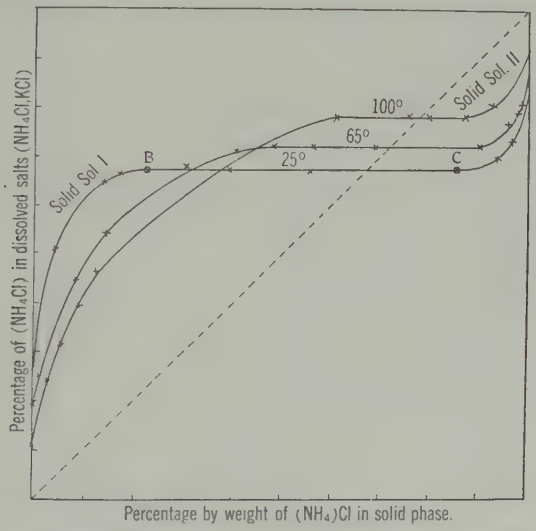

FIG. 32.—The system ammonium chloride-potassium chloride-water, illustrating solid solutions of type IV.

with crystals of Series II is below the diagonal evaporation of solutions containing more than 87 per cent of $(NH_4)Cl$ must cause such systems to move towards C. The entire horizontal portion of the equilibrium curve corresponds to a congruent solution, and the points B and C have the same significance as far as equilibria are concerned. If the diagram used to represent the system expressed the relation between water and the two salts in the liquid phase the resulting solubility curve, unlike those of the three preceding types, would show a break at the point of saturation with the two saturated mixed crystals. This solution must have a minimum fugacity. If the horizontal part of the equilibrium curve is short the differences in the properties of

the two series of solids are small and the break in the solubility curve may be but slight.

The systems KBr-KI-H_2O,[18] KCl-KI-H_2O,[19] $KClO_3$-$TlClO_3$-H_2O [20] and $KMnO_4$-$RbMnO_4$-H_2O [21] belong to this type.

Solid Solutions of Type V. Very few systems of this type have been recognized. The system $HgBr_2$-HgI_2-acetone, investigated by Reinders,[22] belongs here but for an illustration of an aqueous system it is necessary to cite an example in which both the solid solution and the component solid salts are hydrated.

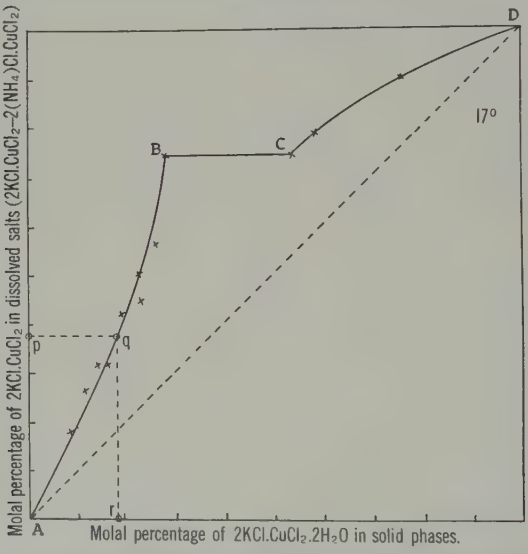

FIG. 33.—The system ammonium cupric chloride-potassium cupric chloride-water, illustrating solid solutions of type V.

The system $(NH_4)Cl$-$CuCl_2$-KCl-H_2O is clearly a four-component system but if the composition of the liquid phase is always such that it can be expressed in terms of the components $2(NH_4)Cl.CuCl_2$ and $2KCl.CuCl_2$-H_2O it becomes three-component. This system, investigated by Fock,[23] is represented in Figure 33. The figure shows that although a portion of the equilibrium curve is horizontal all of it is above the diagonal

[18] Amadori and Pampini, *Atta. Accad. Linc.*, V *21*, II, 477 (1911).
[19] Amadori and Pampini, *l. c.*
[20] Roozeboom, *Z. physik. Chem., 8,* 532 (1891).
[21] Muthmann and Kuntze, *Z. Kryst., 23,* 374 (1894).
[22] Reinders, *Z. physik. Chem., 32,* 598 (1900).
[23] Fock, *Z. physik. Chem., 12,* 658 (1893).

and hence there is neither a congruent point nor a crystallization end point. Evaporation of a solution represented by p yields systems corresponding first to q and then to B, but when this point is reached a new solid appears and further evaporation causes the first solid to react with the solution to form the second solid. After the first solid has been used up further evaporation causes the system to change along C to D. In such systems the solutions saturated as to the two solids do not show the minimum fugacity. They differ from those of Type I only in the appearance of a second solid and a temporary halt in the changes which the composition of the solution undergoes when evaporated at a constant temperature.

Relations Between the Five Types. The form of the equilibrium curves which serve to distinguish systems of the first three types depends upon the position of the points representing saturated solutions, the water in which exhibits a maximum or a minimum fugacity. The composition of these solutions corresponds to minimum or maximum concentrations of all the molecular species which the solutions contain. Minimum values for fugacity are associated with maximum total solubility, maximum degrees of dissociation and a minimum of complex formation.

Systems of the first three types seem to differ fundamentally from the last two but the gap between the two groups is easily bridged. Figure 32 shows that the length of the horizontal portion of the equilibrium curve decreases with increasing temperature and probably becomes zero at slightly above 100°. If so the system changes from Type IV to Type II at this temperature. The system $(NH_4)Cl$-$MnCl_2$-H_2O, investigated by Clendinnin and Rivett,[24] illustrates the same phenomena. In this system there are two series of solids composed of $(NH_4)Cl$ and $MnCl_2.2H_2O$ above 24° and only one below 24°. An inspection of Figure 29 shows that, between 13 and 100 per cent of $(NH_4)_2SO_4$ in the solid phase, a very large change in the composition of the solid phase is associated with a small change in the liquid phase, or that this portion of the curve approaches a horizontal line, which corresponds to a change from Type I to Type V.

Additional types might be suggested but they involve no new features of importance. The system $(NH_4)NO_3$-KNO_3-H_2O,

[24] Clendinnin and Rivett, *J. Chem. Soc., 123,* 1344 (1923).

studied by Caillart,[25] shows two gaps in the continuity of the mixed crystal series and three different solid phases. Systems in which double salts form solid solutions with one of the component salts and those in which two double salts form solid solutions are not rare.

Hydrated Solid Solutions. A large number of mixed crystals contain water of crystallization, but the percentages found are such as to make it obvious that the water is associated with either or both of the other components in a simple stoichiometrical ratio. This relation holds true for such a large number of solids that it seems necessary to assume that the water never enters into their composition as an independent component. Assuming that this relation is a general one the properties of such crystals, like those of anhydrous mixed crystals, can be expressed in terms of a single concentration, and the five types of equilibrium curves already considered should apply to hydrated mixed crystals also. Type I is illustrated by the system $MgSO_4.7H_2O$-$ZnSO_4.7H_2O$-H_2O and Type II by the system $Al_2K_2(SO_4)_4.24H_2O$-$Fe_2K_2(SO_4)_4.24H_2O$-H_2O, investigated by Hollmann.[26]

Dimorphous Series of Solid Solutions. Changes in the degree of hydration of a salt are invariably associated with prominent changes in the crystalline form it assumes as well as in its physical properties including its ability to dissolve other salts. There are no convincing illustrations of solid solutions whose component salts are both hydrated but hydrated differently. It is true that the percentages of water found in some of these solids differ slightly from those required for equal hydration, but it is customary to attribute these discrepancies to occlusion of the mother liquor from which they separated. In general unless the two salts are capable of existing in the same degree of hydration over a similar range of temperatures, and unless the two hydrates possess similar crystallographic properties, a continuous series of solid solutions is not possible. There are however many examples of solid solutions composed of a hydrated and an anhydrous salt. The systems $(NH_4)Cl$-$FeCl_2$-H_2O,[27] $(NH_4)Cl$-$NiCl_2$-H_2O [28] and $(NH_4)Cl$-$MnCl_2$-H_2O [29] might be cited.

[25] Caillart, *Bull. Soc. Mineral.* (Paris), *41*, 25 (1918).
[26] Hollmann, *Z. physik. Chem.*, *37*, 204 (1901); Hollmann, *l. c.*, 202.
[27] Clendinnin, *J. Chem. Soc.*, *121*, 802 (1922).
[28] Clendinnin, *l. c.*, 802.
[29] Clendinnin and Rivett, *J. Chem. Soc.*, *119*, 1332 (1921).

Much more numerous are illustrations of systems which yield two series of solid solutions which differ as to hydration. The system $CoCl_2$-$MnCl_2$-H_2O studied by Stortenbecker,[30] is typical. It is represented by Figure 34. One series of solid solutions is red and contains from 0 to 37 per cent of $MnCl_2.6H_2O$; the other series is violet and contains from 74.5 to 100 per cent of $MnCl_2.4H_2O$. Both series exist in a metastable form at concentrations in excess of these limits, and it is possible that the curves for both series could have been followed from one pure salt to the other by careful experimental work.

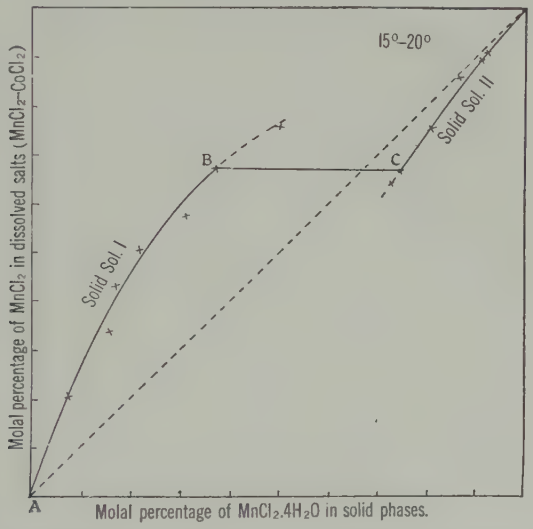

FIG. 34.—The system cobaltous chloride-manganous chloride-water, illustrating dimorphous solid solutions.

Transformation Temperatures of Hydrated Solid Solutions. The system Solid Sol. I-Solid Sol. II-liquid-vapor is not fixed unless the temperature is fixed, and therefore the composition of the saturated solution can be varied by changing the temperature. If the temperature is altered without at the same time altering the composition of the solids one of them must disappear. This is merely another form of the statement that the temperature at which one solid changes to the other depends upon their composition, or that every possible pair of such solids has a

[30] Stortenbecker, *Z. physik. Chem., 16,* 256 (1895).

definite transformation temperature. Salts capable of forming two continuous series of solids, which differ as to crystalline form or as to both crystalline form and degree of hydration should show a continuous series of transformation temperatures, extending from that of one pure component to that of the other. Very few experimental data regarding such systems are available. The system $CuSO_4$-$MnSO_4$-H_2O, as shown by Hollmann,[31] which yields a continuous series of monoclinic crystals with seven molecules of water and a continuous series of triclinic crystals with five molecules of water, gives a transition temperature curve with a maximum as shown in Figure 35. The composition of the two

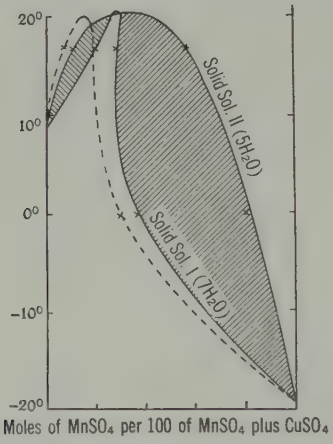

FIG. 35.—The system cupric sulfate-manganous sulfate-water, from −20° to 20°.

solids and of the liquid which are in equilibrium at 0° and at 17°, and the transition temperature of pure $MnSO_4.7H_2O$ are the only data, but these values indicate that the changes in the composition of the two salts are correctly represented by the full lines, and that of the solution by the dotted lines of the figure, and that there is a maximum transition temperature of about 20°. There are comparatively few illustrations of systems composed of salts which form two continuous series of isomorphous hydrates but the number of systems in which isodi- or isotrimorphous hydrates are concerned is large and varied. Hollmann [32]

[31] Hollmann, *Z. physik. Chem., 54,* 105 (1905).
[32] Hollmann, *Z. physik. Chem., 50,* 567 (1904).

showed that fourteen types of diagram representing such systems were possible and cited illustrations of many of these types. A single illustration represented by Figure 36 will be considered here. In this diagram the dotted lines represent the composition of liquid and the full lines that of saturated solid phases. The latter divide the entire area into fields which mark the temperature and composition limits of each of the five series of solid solutions. The shaded areas represent gaps in the continuity of

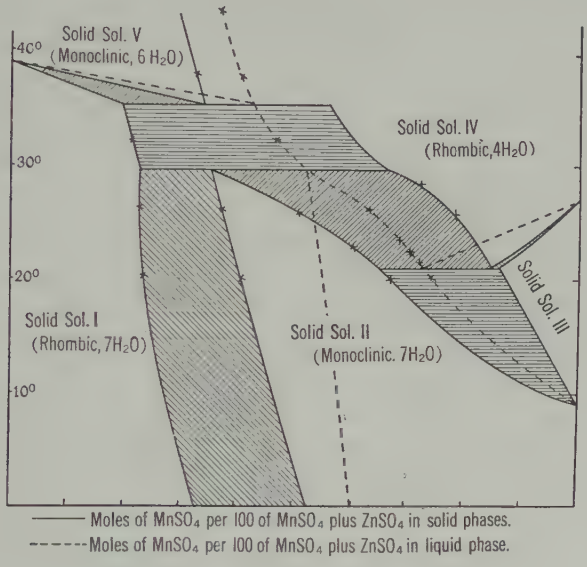

FIG. 36.—The system manganous sulfate-zinc sulfate-water from 0° to 40°.

these series, and therefore mixtures of two different kinds of solids. It will be noted that at 29° three different solids are in equilibrium with the same solution, and below this temperature two pairs of the three solids, each pair in equilibrium with a solution of definite composition, are in equilibrium. Similar nonvariant systems exist at 35° and at 22°.

Vapor Pressures of Hydrated Solid Solutions. Very few measurements of vapor pressures of solid solutions have been made and in most of these little attention has been paid to the nature of the second solid concerned. Hollmann [33] found two

[33] Hollmann, *Z. physik. Chem., 37,* 202 (1901).

clearly defined maxima for the vapor pressures of the $(Zn,Mg)SO_4.7H_2O$ series and one for the $(Fe,Al)_2K_2(SO_4)_2.24H_2O$ and the $(Cr,Al)_2K_2(SO_4)_2.24H_2O$ series. The maxima of the series first named correspond in composition to minima found on the transition temperature curve. One of these points corresponds exactly to the composition represented by the formula $2MgSO_4.ZnSO_4.7H_2O$, the other to $MgSO_4.ZnSO_4.7H_2O$. The conclusion seems inevitable that double salts may be concerned in the formation of solid solutions even when the two components form what seems to be a continuous series.

Partition Constant for Solid and Liquid Phases. The fundamental assumption made by van't Hoff in his treatment of solid solutions was that there was a perfect analogy between the properties of solid and liquid solutions of low concentration. Hence there should be a simple numerical relation between the concentrations of a solute in the liquid and solid phases which are in equilibrium and it should be possible to determine experimentally "partition coefficients" similar to those found by Nernst [34] for pairs of consolute liquids. The validity of such a relation depends primarily upon the nature of the molecular species present in the two solutions. It should not be true unless either all of the component concerned is present in the same form in both solutions, or the same proportions of it exist in the two solutions in the same forms, that is, the component is dissociated or aggregated to the same degree. Reliable measurements of the actual condition of the solute in both solid and liquid phases are scarcely possible and hence any experimental work designed to test this relation is open to serious criticism. Certain results with solid solutions of nonpolar components show fairly uniform values for the assumed constant. This was found for solution of thiophene in benzene,[35], piperidene in benzene [36] and with less accuracy for dilute solutions of para-dibrom benzene in para-dichlor benzene.[37]

For solid solutions of binary electrolytes in equilibrium with aqueous solutions Fock [38] proposed the formula

$$C[1 + \alpha(\sqrt{x} - 1)] \div x = K$$

[34] Nernst, *Z. physik. Chem., 8,* 110 (1891).
[35] Beckman and Stock, *Z. physik. Chem., 17,* 120 (1895); *17,* 612 (1897).
[36] Bruni, *Gazz. Chim. Ital., 28,* I, 259 and 277 (1897).
[37] Meyer, *Rec. Trav. Chim., 42,* 310 (1923).
[38] Fock, *Z. Kryst., 28,* 353 (1897).

in which C represents the molal concentration of the component in the liquid and x of the same component in the solid phase and α the degree of dissociation of this component in the liquid. He did experimental work upon a number of systems of this type using values for α based upon conductance measurements but did not obtain satisfactory concordance for the value of K. Meyer [39] also failed to obtain confirmation of this formula in his study of the systems potassium chromate-potassium sulfate-water and lead bromide-lead chloride-water.

[39] Meyer, *Rec. Trav. Chim., 42,* 304 (1925).

Chapter VI.

Systems Derived from Water and Two Electrolytes Which Yield One Hydrogen Ion, or One Hydroxyl Ion, or Both.

Systems Derived from a Salt and an Acid with a Common Anion and Water. The important difference between these systems and those considered in the preceding chapters arises from the fact that many acids, especially the strong inorganic acids, are very soluble and it is only at temperatures below zero that saturation with them or their various hydrates becomes possible. Where halogen acids are concerned the partial pressures of these acids in the vapor phases are important features of such equilibria, but there are few experimental data available in which measurements of these pressures have been made. The new solid phases which may result from the addition of an acid to a system composed of a salt of these acids and water are either lower hydrates or acid salts. The lower hydrates or anhydrous salts may result from a reduction in the pressure of the water vapor in equilibrium with the solution to a value below that required for the existence of the original hydrate as a stable solid phase. Acid salts are in all essential respects analogous to double salts and their treatment does not present any new features. The solubility curves representing saturation as to acid salts are frequently less symmetrical with respect to the axes of reference than those of typical double salts, which is probably the result of the presence of large concentrations of complex ions containing hydrogen in the liquid phase.

The system hydrogen sulfate-lithium sulfate-water, which was studied by van Dorp[1] at a temperature of 30°, is fairly typical of such systems. The data obtained are represented by means of an equilateral triangle in Figure 37. The composition of the

[1] van Dorp, *Z. physik. Chem., 73,* 289 (1910).

solid phases concerned was ascertained to be $Li_2SO_4.H_2O$, Li_2SO_4 and $Li_2SO_4.H_2SO_4$, the respective solubility curves for which are represented by the lines AB, BC and CD although there is no definite evidence of any break in the curve at B as required by the phase rule. The absence of additional solid phases was confirmed by use of the residue method of Schreinemakers, for it will be noted that the tie-lines connecting points on the solubility curves and points representing mixtures of these solutions and the solids with which they are in equilibrium all con-

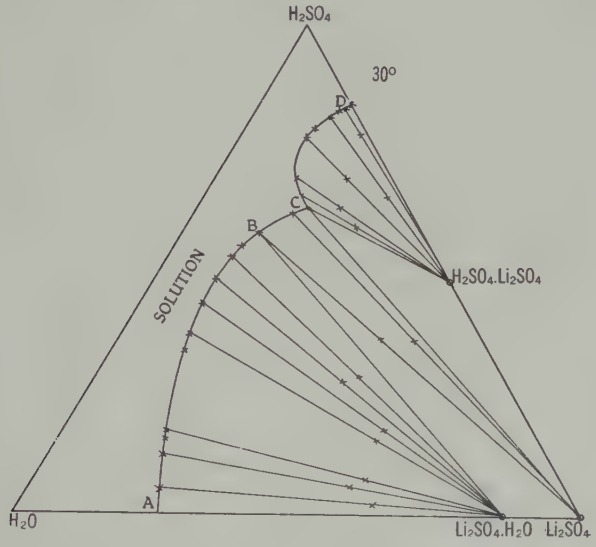

FIG. 37.—The system hydrogen sulfate-lithium sulfate-water at 30°.

verge toward the points representing the composition of the three solids named. The line joining the points representing the solid $Li_2SO_4.H_2O$ and pure water meets the solubility curve, representing saturation as to the solid named at A, which is therefore a congruent point. Similarly the line joining the points representing the solid $Li_2SO_4 . H_2SO_4$ and pure H_2SO_4 meets the curve representing saturation as to this solid at D, and this is also a congruent point. There are no other points on the composite solubility curve of which corresponding statements can be made. The point D moreover is the only crystallization end point. It will be noted that on account of the large solubility of sulfuric

acid the area of the diagram which represents unsaturated solutions differs from that of the diagrams hitherto considered in that it includes the entire side of the diagram. The remaining area of the triangle is divided into five spaces representing either solutions of variable composition in equilibrium with one of the three solids or solutions of fixed composition, either B or C, saturated as to two solids, either $Li_2SO_4.H_2O$ and Li_2SO_4 or Li_2SO_4 and $Li_2SO_4.H_2SO_4$.

Systems Derived from a Salt and a Base with a Common Cation and Water. The strong bases do not possess the very large solubility of the strong acids and most of the weak bases are only moderately or slightly soluble. The solid phases to be looked for in such systems are either the base itself or some of the hydrates, the salt or one or more of its hydrates and "basic salts." Basic salts can be treated as double salts and the diagrams representing such systems present no unusual features.

Systems Derived from an Acid, a Base and Water. These systems yield four different ions but since water can be derived from two of these ions it is not necessary to include water as a component, and such systems are therefore three-component systems. As the sum of the positive ions must equal the sum of the negative ions such systems may be defined in terms of three ions, namely hydrogen ion, hydroxyl ion and either the other anion or the other cation. It is also possible and often preferable to define such systems in terms of the acid or its anhydride, the base or its anhydride and water. It will be noted that these systems include both of those included in the two preceding groups, that is systems whose composition may vary from that of pure acid and water to pure salt and water, in addition to those whose composition can vary from that of pure salt and water to pure base and water. The usual reason for considering separately the two groups of systems under consideration is that data relating to only one of them are available.

Several schemes for the graphical representation of these systems are in use. A pair of rectangular axes such as those of Figure 38 possesses some advantages. The vertical axis OY here represents concentration of salt; the horizontal axis measured on the left, that is along OX, represents acid; the horizontal axis measured to the right, that is along OZ, base. The solubility curve which has been drawn is purely imaginary. The AB portion of

it is assumed to represent solutions saturated as to the acid, its anhydride or one of its hydrates; similarly, the BC portion might represent solutions saturated as to an acid salt; the CD portion solutions saturated as to the normal salt; the DE portion solutions saturated as to a basic salt and the EF portion solutions saturated as to the base, its anhydride or one of its hydrates. For most purposes it will be found advantageous to condense such diagrams by the elimination of the salt as a separate component and to reduce the angle between OY and OZ from 180° to 90°. From the point of view of the phase rule this simplification is necessary if the mixtures represented by the diagram are to be treated as a single system.

The System Strontium Oxide-Hydrogen Chloride-Water. The convention indicated in the preceding paragraph has been

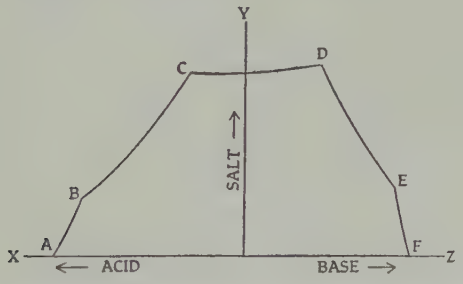

FIG. 38.—Hypothetical diagram for the system acid-base-water.

adopted in representing the system strontium oxide-hydrogen chloride-water, which was investigated by Milikan,[2] as shown in Figure 39. The dotted line extending from O through Q represents all possible mixtures derived from SrO and HCl in the molal ratio of 1 : 1 and therefore includes, as the result of the elimination of water, the compound Sr_2OCl_2. The dotted line extending from O through S represents all such mixtures in which the molal ratio is 1 : 2, and therefore includes the compound $SrCl_2$. The points P, Q, R and S correspond to the composition of the four solids which are present in this system at 25°. The AB portion of the solubility curve represents saturation as to $SrO.9H_2O$, the BC portion as to $SrO.SrCl_2.9H_2O$, the CD portion as to $SrCl_2.6H_2O$ and the DE portion as to $SrCl_2.2H_2O$. The

[2] Milikan, *Z. physik. Chem., 92,* 504 (1918).

OQ line cuts the solubility curve AB and the point of intersection cannot be a congruent point. The OS line meets the extreme end of the solubility curve CD at C and this point is a congruent point. Further, since C is at the end of the solubility curve CD it is a crystallization end point for solutions represented by points above OC but not for those represented by points below OC. Owing to the slight solubility of $SrCl_2.2H_2O$ in solutions containing large concentrations of HCl, the curve CDE seems to meet the horizontal axis of the diagram. If the latter had been

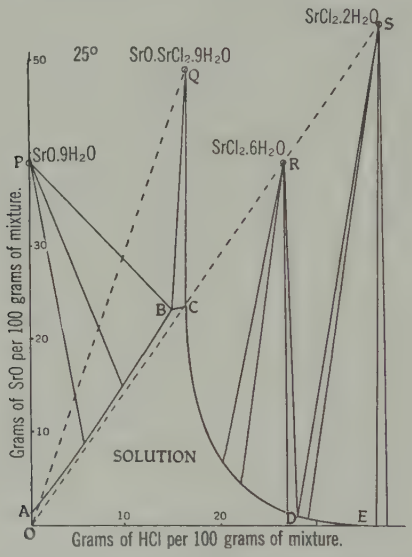

FIG. 39.—The system hydrogen chloride-strontium oxide-water.

drawn to a larger scale it could have been shown that this is not true and the limits of the field marked "solution" are not defined by the data now available. By working in closed vessels still higher concentrations of HCl could be obtained and additional solid phases, each associated with a definite solubility curve, should be obtained. The new solids might include still lower hydrates of $SrCl_2$, acid salts and either HCl or some hydrate of HCl.

The System Potassium Oxide-Phosphorus Pentoxide-Water. This system, studied by D'Ans and Schreiner [3] and also by

[3] D'Ans and Schreiner, *Z. physik. Chem., 75,* 103 (1910).

Parker,[4] is more complicated than the one previously considered. It has been represented in a similar manner in Figure 40. Salts of three degrees of basicity, namely, $3K_2O.P_2O_5$, $K_2O.P_2O_5$ and $K_2O.2P_2O_5$, whose respective compositions correspond to points on the three broken lines OQ, OR and OS, are present as solid phases. The first of these exists as a hexahydrate, in contact with solutions represented by the curve ABC, and as an anhydrous salt in contact with solutions represented by the curve

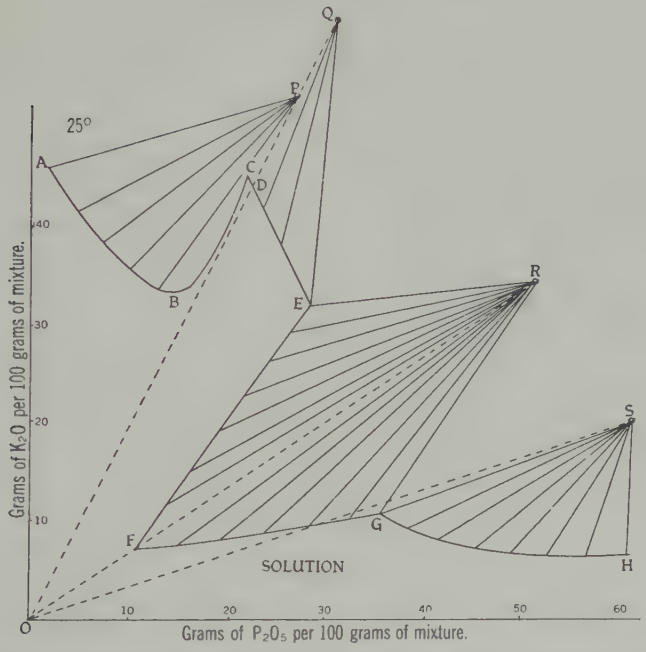

FIG. 40.—The system phosphorus pentoxide-potassium oxide-water at 25°.

CDE. The second salt exists as a dihydrate in contact with solutions represented by points on EFG and the third as a pentahydrate in contact with solutions along GH. The line OQ intersects the solubility curve CE at D and this is a congruent point but not a crystallization end point. The line OR intersects the solubility curve EFG at F which seems to mark a clearly defined change in the direction of the curve. Such a break should be associated with a change in the nature of the solid phase. Since

[4] Parker, *J. Phys. Chem., 18,* 654 (1914).

there is no doubt that the same solid is in equilibrium with the solutions on either side of F it is probable that the curve is actually continuous at this point. This point is also a congruent point but not a crystallization end point. The line OS intersects the solubility curve FG but as the solid and liquid phases at this point contain different proportions of K_2O and P_2O_5 this is neither a congruent point nor a crystallization end point, and the compound $K_2O.P_2O_5.5H_2O$ is not stable in water. The only crystallization end point on the solubility curve is at E.

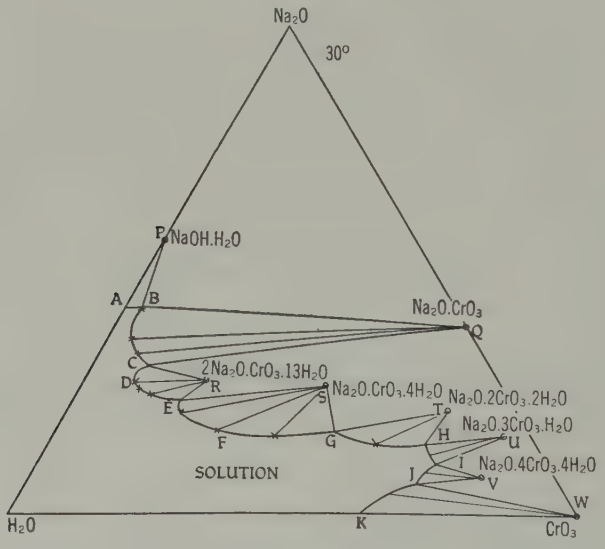

FIG. 41.—The system chromium trioxide-sodium oxide-water at 30°.

The System Chromium Trioxide-Sodium Oxide-Water. A still more complex system, which was studied by Schreinemakers,[5] is derived from chromium trioxide, sodium oxide, water. The data obtained for the system at 30° are represented in Figure 41. The solubility curve is composed of eight branches each of which corresponds to a different solid. Two of these represent the component electrolytes, the other six represent salts which exhibit five different degrees of basicity. The curve BC represents saturation as to $Na_2O.CrO_3$ and EFC as to the tetrahydrate of the same salt. The curve CDE which separates those named is

[5] Schreinemakers, *Z. physik. Chem.*, *55*, 93 (1906).

saturated as to a more basic solid having the composition $2Na_2O.CrO_3.13H_2O$. This is a very unusual relation in that the more basic salt is stable when in contact with solutions containing a smaller concentration of base. It follows that the addition of a small amount of CrO_3 to a saturated solution of $NaOH.H_2O$ will give rise to the more basic $2Na_2O.CrO_3.13H_2O$. It might be suggested that $2Na_2O.CrO_3.13H_2O$ is metastable and that the curves BC and CFE actually intersect. Schreinemakers was able to obtain one point on the extension of BC beyond C and also one on the extension of CFE beyond E, but both systems were metastable. The occurrence of this compound as a stable solid phase is found in the work of Mylius and Funk.[6] A more probable explanation is that this compound is less soluble than $Na_2O.CrO_3$ even in solutions containing large concentration of NaOH but that owing to the large degree of hydration it cannot exist in contact with solutions saturated as to $NaOH.H_2O$.

The relative basicities of the six salts which appear as solid phases are shown by lines joining the H_2O apex with points on the Na_2O-CrO_3 side of the triangle corresponding to $2Na_2O.CrO_3$, $Na_2O.CrO_3$, $Na_2O.2CrO_3$, $Na_2O.3CrO_3$ and $Na_2O.4CrO$ respectively. The first of these lines intersects the solubility curve CDE very near E. This point is therefore a congruent point and the solid $2Na_2O.CrO_3.13H_2O$ is stable in water. The second, which passes through S and ends at Q, intersects the solubility curve EFG, which fixes the position of a congruent point and shows that the solid $Na_2O.CrO_3.4H_2O$ is stable in water. The third passes through T and intersects the curve GH near G; this locates the position of a third congruent point and shows that the solid $Na_2O.2CrO_3.2H_2O$ is stable in water. The fourth passes through U, intersects the curve HI near H; this locates a fourth congruent point and shows that $Na_2O.3CrO_3.H_2O$ is stable in water. The fifth passes through V and intersects the curve IJ very near T; this locates a fifth congruent point and establishes the fact that the solid $Na_2O.4CrO_3.4H_2O$ is stable in water. It is obvious that A and K also represent congruent points and between each successive pair of congruent points on the composite solubility curve, that is at B, E, C, H, I and J are crystallization end points.

[6] Mylius and Funk, *Abhand. Phys. Tech. Reichanstalt,* III 499 (1900).

Chapter VII.

Four Component Systems Derived from Water and Three Electrolytes Which Yield a Common Ion.

The Variables Concerned. Systems derived from water and three electrolytes, all of which yield a common anion or cation, but which do not form insoluble compounds as a result of hydrolysis, are clearly four-component systems. The maintenance of such systems under ordinary atmospheric conditions, as in the systems already considered, affects the equilibria concerned to a negligible degree only and is usually disregarded. This statement assumes that the molal solubility of the components of the atmosphere in the liquid and solid phases is extremely small, that the electrolytes are not appreciably volatile and that the total pressure is constant although the partial pressure of the water vapor varies.

The number of solids to be considered may be large. In addition to ice and the three simple electrolytes they include as possibilities one or more hydrates of each of these electrolytes, both double and triple salts and double and triple solid solutions all of which may be hydrated. The maximum possible number of concentration variables concerned in each of the solid phases is three; since however water does not enter into the formation of solid solutions as an independent component only two are actually concerned. The maximum number of concentration variables concerned in the liquid phase is three, but in the vapor phase, if the concentration of water vapor is expressed as a partial pressure, there are none unless one or more of the electrolytes is appreciably volatile. A system composed of vapor, liquid and four solids is invariant and can exist as a stable system only at some specific temperature and pressure. Reducing the number of phases by one makes it possible to fix arbitrarily the temperature, the partial pressure of the water vapor or any one of the

concentration variables, provided all of the other variables are given the values which the equilibrium conditions of the system demand.

The Use of a Regular Tetrahedron in Graphical Representation. An entirely satisfactory graphical method for the representation of four-component systems would be one in which the variations in the concentrations of the four components of the liquid phase and in temperature and pressure could be represented. As the variation in pressure is of minor importance and is difficult to determine and fix arbitrarily, it can usually be disregarded. The temperature factor is of extreme importance, but since experimenters often find it desirable to limit their determinations to a few standard temperatures it is customary to prepare a corresponding number of isothermal diagrams.

A regular tetrahedron, that is a tetrahedron all of whose edges and facial angles are equal, possesses geometric properties which make it of especial value for the representation of such systems. Its four solid apices may represent the position in space of the four pure components, its six edges mixtures of each of the six pairs of two components taken separately, and its four faces mixtures of each of the four groups of three components taken separately. The four one-component, six two-component and four three-component systems, which represent the limiting values of the more complex four-component system, all find their proper location in such a figure, and are all capable of being expressed in terms of the same numerical units, namely, the edge of the tetrahedron. If from some point within the space enclosed by the faces of a regular tetrahedron such as O of Figure 42, lines be drawn parallel to the six edges until they intersect the four faces, it will be found that four smaller regular tetrahedrons will be outlined. Each of these has the common apex at O and one face in common with one of the faces of the larger tetrahedron. It can be shown geometrically that the sum of the edges of the four smaller tetrahedrons, that is $OA + OJ + OD + OH$ equals the edge of the larger one. Further, if the position of any point within the tetrahedron be expressed in terms of the distance between it and the four faces, the sum of these distances must equal the edge of the tetrahedron provided all measurements are made along lines parallel to the proper edge of the tetrahedron. Hence the position of points within the tetrahedron, which represents

a four-component system, can also be expressed in terms of the same unit as that suggested for the simpler systems. In the figure OABC, ODEF, OGHI and OJKL represent faces of the four smaller tetrahedrons, and the position of the point O is defined by its distance from the face WQR along OA, from WPQ along OD, from PQR along OH and from WRP along OJ.

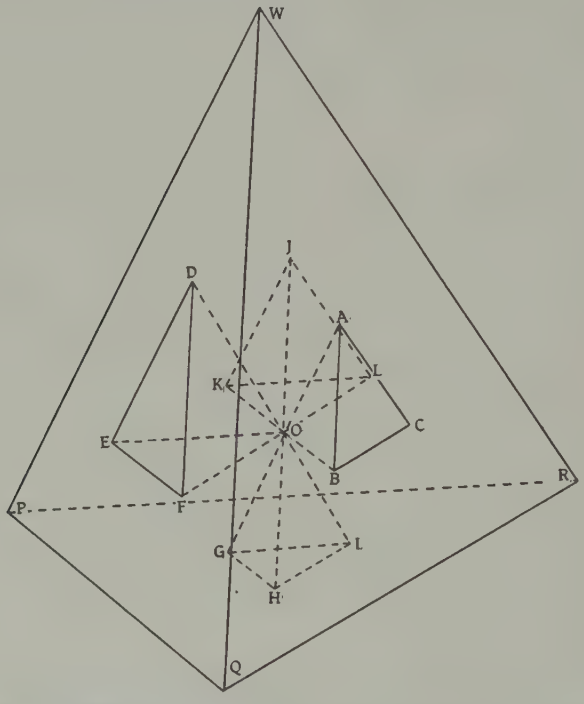

FIG. 42.—Illustrating the use of a regular tetrahedron in representing four-component systems.

The System Ammonium chloride-Barium chloride-Cupric chloride-Water. The use of a regular tetrahedron in representing the system $(NH_4)Cl$-$CuCl_2$-$BaCl_2$-H_2O, investigated by Schreinemakers,[1] is indicated in Figure 43. The three vertices which limit the horizontal face upon which the tetrahedron rests, represent the three anhydrous salts and the remaining vertex, water. The solid phase $BaCl_2.2H_2O$ finds its proper place at L on the H_2O-$BaCl_2$ edge, the solid phase $CuCl_2.2H_2O$ at M on

[1] Schreinemakers, *Z. physik. Chem.*, *66*, 690 (1909).

the H_2O-$CuCl_2$ edge and the double salt $2(NH_4)Cl.CuCl_2.2H_2O$ at N in the face $(NH_4)Cl$-$CuCl_2$-H_2O. The points L, M and N together with the points representing $(NH_4)Cl$ and H_2O outline the limits of that portion of the tetrahedron which correspond to equilibria which have been experimentally realized at the chosen temperature. Below these limits the three hydrated salts and

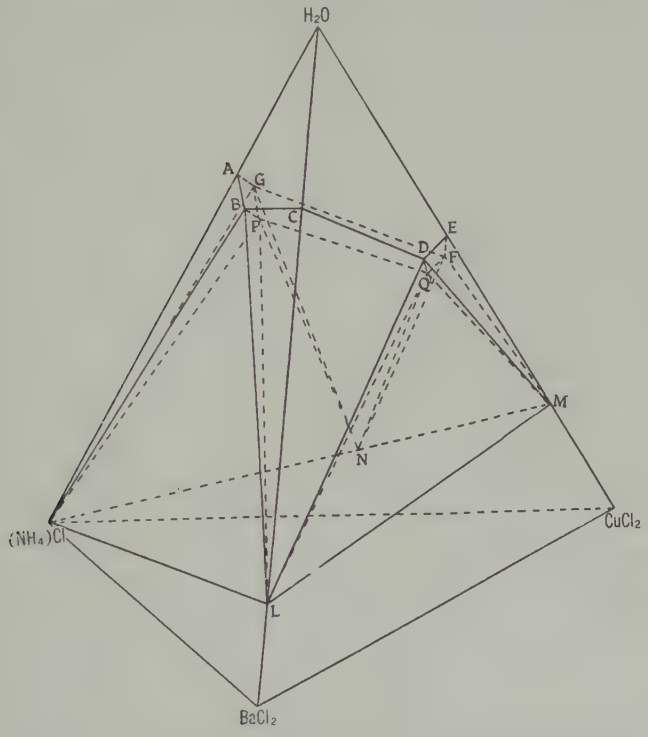

FIG. 43.—The system ammonium chloride-barium chloride-cupric chloride-water.

$(NH_4)Cl$ are concerned. Similarly the solubility curve for the system $(NH_4)Cl$-$BaCl_2$-H_2O is represented by ABC, that for $BaCl_2$-$CuCl_2$-H_2O by CDE and that for $(NH_4)Cl$-$CuCl_2$-H_2O by EFGA. Points representing saturation as to three solids, namely $(NH_4)Cl$-$2(NH_4)Cl.CuCl_2.2H_2O$-$BaCl_2.2H_2O$ and $2(NH_4)Cl.CuCl_2.2H_2O$-$BaCl_2.2H_2O$-$CuCl_2.2H_2O$ correspond to the points P and Q respectively within the tetrahedron. These nine points outline the limits of four surfaces which separate the

space within the tetrahedron representing unsaturated solutions from a number of spaces representing more complex systems. The space limited by the point representing $(NH_4)Cl$ and the surface ABPG represents varying proportions of solid $(NH_4)Cl$ and saturated solution; that limited by the point L and the surface BCDQP, solid $BaCl_2.2H_2O$ and saturated solution; that limited by the point M and the surface DEFQ, solid $CuCl_2.2H_2O$ and saturated solution; that limited by the point N and the surface FGPQ, solid $2(NH_4)Cl.CuCl_2.2H_2O$ and saturated solution.

Projection of the Tetrahedral Diagram. Although the representation of simple four-component systems by the method indicated in the preceding paragraphs gives an easily understandable picture of the system when drawn perspectively, the numerical constants corresponding to any point within the diagram cannot be obtained directly from such a drawing. It is customary therefore to project the space figure on one or more planes, either from an infinite distance, that is orthogonally, or from a point on or near the diagram, that is clinographically. The plane which includes the apices representing the three salts is the logical one to use for such systems, and the orthogonal projection gives a diagram in which the proportions of all four components are correctly represented. Very little difficulty will be experienced in making this projection for it can be shown geometrically that the proper location of a point on the projection plane is obtained by adding one-third of the distance representing the water to each of the distances representing the other components associated with the water. This procedure has been applied to the system just considered and the result appears in Figure 44. The point representing pure water corresponds to the center of the triangle, that representing solid $(NH_4)Cl$ corresponds to an apex of the triangle. The point representing $BaCl_2.2H_2O$ should express the composition 85.25 per cent $BaCl_2$ and 14.75 per cent H_2O, and hence appears on the projection as $85.25 + \frac{1}{3}(14.75)$ or 90.70 $BaCl_2$ which corresponds to L. Similarly the point representing $CuCl_2.2H_2O$ corresponds to $78.89 + \frac{1}{3}(21.11)$ or 85.93 $CuCl_2$ which is represented by M; the point representing $2(NH_4)Cl.CuCl_2.2H_2O$ corresponds to $38.55 + \frac{1}{3}(12.98)$ or 42.88 $(NH_4)Cl$ and $48.47 + \frac{1}{3}(12.98)$ or 52.80 $CuCl_2$ which is represented by N. In like manner the solutions saturated as to one, two or three solid phases have been properly represented, the

letters used corresponding to those used in Figure 43. When these points are properly connected the resulting lines outline four irregularly shaped fields, each of which represents solutions saturated as to one of the four solids.

It is a simple task to locate on this projection the approximate form of the crystallization paths representing the changes in composition which would result from evaporation of solutions at the chosen temperatures. The principle used has already been noted,

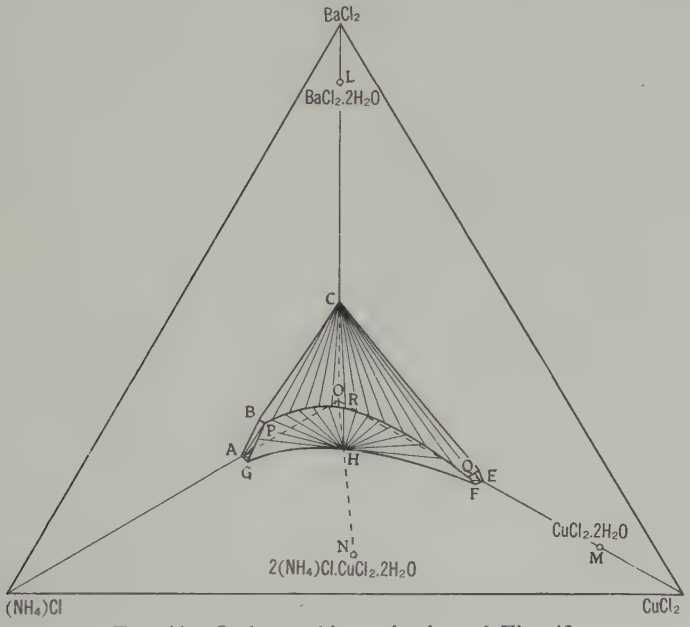

FIG. 44.—Orthographic projection of Fig. 43.

namely to draw lines from that point which represents the composition of solutions saturated as to each pure solid across the area representing all possible solutions saturated with the solid. The directions of these one-solid paths clearly indicate that there are two crystallization end points, namely P and Q, at which three solid phases are present. There must also be a congruent point on the PQ line, which can be located easily. The point H at the intersection of FG and NO represents solutions saturated with pure double salt. The point C represents solutions saturated with $BaCl_2.2H_2O$ and the line joining C and H represents mix-

tures of the two saturated solutions. Its intersection with PQ which represents all possible solutions saturated as to the double salt and $BaCl_2.2H_2O$, that is R, must represent the desired congruent point.

It should be noted that exactly the same diagram would have been obtained if the percentages of the three salts representing any mixture had been measured from the central point of the triangle on the three axes extending from this point to the three vertices. The preceding discussion explains and justifies the simpler procedure.

Certain diagrams may yield projections, the various fields of which are more clearly defined if some other plane of reference than the one chosen in the illustration is employed. Schreinemakers [2] has made some use of a plane which is parallel to two opposite edges of the tetrahedron, that is orients it as though resting on one of the edges rather than on one of the faces as in the projection described above.

Use of a Pyramid in Graphical Representation. Many investigators prefer to express the composition of the system in terms of the number of grams, moles or equivalents per standard amount of water. If this method is employed the three ratios needed to express the composition of a four-component system containing water can be referred to three axes intersecting in space at any angle except 120°. If the three axes all intersect at an angle of 60° the resulting figure forms the upper portion of a regular tetrahedron, but since one or more of these axes may be of infinite length its properties differ from those of the diagrams already discussed. It is not easy to draw accurately such a diagram in perspective but it can be represented on a plane surface very easily. If the three axes actually intersect in space at equal angles the figure may be conventionally represented by three axes intersecting at 120°, and this procedure has many advantages. Extended use has been made, especially by van't Hoff, of a system of two axes intersecting at 90° and a third at 135°.

The use of the first named procedure is shown in Figure 45, which represents the system magnesium sulfate-potassium sulfate-sodium sulfate-water at 35°, investigated by D'Ans.[3] The median

[2] Schreinemakers, *Z. physik. Chem., 66,* 692 (1909).
[3] D'Ans, *Kali, 9,* 218 (1915).

axis here represents equivalents of $MgSO_4$ per 1000 moles of water, the one to the right K_2SO_4 and the one to the left Na_2SO_4. The line ABCD represents the solubility curve of the three-component system Na_2SO_4-$MgSO_4$-H_2O, the line DEFG that of the system $MgSO_4$-K_2SO_4-H_2O and the line GHIA that of the system K_2SO_4-Na_2SO_4-H_2O. The point O represents pure water and the space limited by it and by the three tetrahedral planes represents unsaturated solutions. Saturation with respect

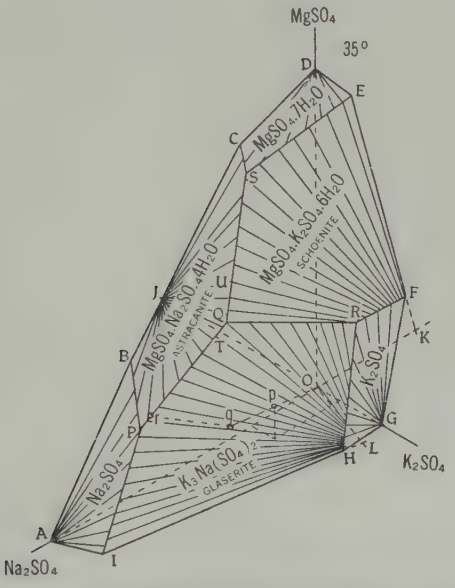

FIG. 45.—The system magnesium sulfate-potassium sulfate-sodium sulfate-water at 35°.

to three sets of solid phases is represented by the points P, Q, R and S, and when these points are properly connected with each other and with the points representing saturation as to two solids, namely, B, C, E, F, H and I, six surfaces are outlined each of which represents all possible solutions saturated respectively with Na_2SO_4, K_2SO_4, $MgSO_4.7H_2O$ and one of the three double salts. These double salts, all of which are minerals found in the Stassfurt salt deposits, are schönite ($MgSO_4.K_2SO_4.6H_2O$), astracanite ($MgSO_4.Na_2SO_4.4H_2O$) and glaserite ($3K_2SO_4.Na_2SO_4$).

The crystallization paths for the Na_2SO_4 surface must radiate from A, those for $MgSO_4.7H_2O$ from D and those for K_2SO_4 from G. The point representing saturation as to pure astracanite is located at the intersection of BC and the line which bisects the angle between the Na_2SO_4 and the $MgSO_4$ axes, that is at J, and the paths for the surface saturated with astracanite must radiate from J. The point representing saturation as to pure schönite is found by a similar construction to be located at K on the prolongation of EF and the paths for the surface representing saturation as to this salt radiate from K. Similarly the paths for the glaserite saturation surface must radiate from L. The general trend of one-solid crystallization paths on the six surfaces indicates that P and S are crystallization end points, and hence congruent points. It can also be shown that there is a third congruent point on PQ and a fourth on QS. The line PQ represents a series of points saturated as to both glaserite and astracanite. The location of this line with respect to the points representing saturation as to pure glaserite and pure astracanite suggests that there may be a point on this line whose composition is that of water plus a mixture of glaserite and astracanite in some unknown ratio. If so it must be a congruent point whose position may be located by a geometric method. It is necessary to first project the space figure on a plane representing zero water, that is to find the location of points representing mixtures of constant amounts of the three salts in their proper proportions. The projection obtained when the sum of the three salts is made 100 is given by the heavy black lines of Figure 46. In constructing this figure the point representing 100 equivalents of Na_2SO_4 is located on OA 100 units of distance from O, 100 of $MgSO_4$ on OD and 100 of K_2SO_4 on OG. The other points on the periphery of the space figure are projected by joining O with the point in question and prolonging the line until it intersects a side of the triangle. Thus B′ represents 100 equivalents of a mixture containing the same proportions of Na_2SO_4 and $MgSO_4$ as B but no water. Points within the space figure are more difficult to project. To find the projection of P draw OP for 100 units of length from O. The total number of equivalents of mixed salts represented by P is 79, which corresponds to W on the Na_2SO_4 axis. Then if 79 units on this axis corresponds to P, 100 would correspond to P′, that is the point at which the line drawn through

the point representing 100 units parallel to WP intersects the prolongation of OP. The other points are projected in a similar manner. We can now locate the point on PQ which represents a mixture of glaserite and astracanite, for the projection of this point must be where the projection of PQ intersects the projection of the glaserite-astracanite line, that is at T′, hence T corresponds to the intersection of PQ and OT′. In a similar manner it is possible

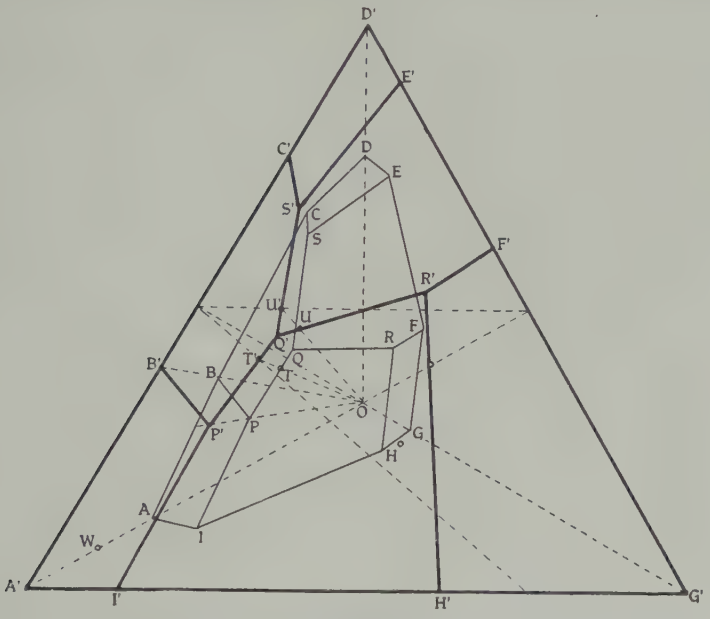

FIG. 46.—Illustrating geometric method of locating congruent points on a diagram.

to locate the fourth congruent point at U on QS. Further, since T and U are congruent points Q must be a crystallization end point.

It might also be noted that although HR and RF separate fields representing saturation with two solids they are not crystallization paths. The one-solid crystallization paths which radiate from G pass across these lines into the adjoining fields, and not along them. Any K_2SO_4 which may have separated is transformed into the new solid before the new field is entered.

The type of diagram of which Figure 45 is an illustration can

be elaborated further for the purpose of indicating the limits of the spaces representing mixtures other than saturated solutions. There is one columnar space extending from the surface ABPI along the OA axis for an indefinite distance, which represents Na_2SO_4 and saturated solutions, and a second extending from the surface FGHR along the OG axis, which represents K_2SO_4 and saturated solutions. An oblique pyramid, extending from surface CDES to some point on the OD axis, represents $MgSO_4.7H_2O$ and saturated solution. Similarly the spaces representing astracanite and saturated solution extend from a point on the ABCDO plane to the BPQSC surface; that representing schönite and saturated solution extends from a point on the DEFGO plane to the ESQRF surface. Finally a columnar space extends from the HIPQR surface for an indefinite distance parallel to OL which represents glaserite and saturated solution. The location of spaces representing mixtures of two solids and a saturated solution, or of three solids and a saturated solution of constant composition can be expressed in terms of the spaces whose locations have already been specified. Such a diagram can then be used for the purpose of ascertaining the probable composition of any mixture of the four components except an unsaturated solution. The same information can be obtained by use of the projected diagram of Figure 46. It will be found, however, that this diagram is identical with that which would have been obtained by the method of Jänecke, which will be explained in a later section of this chapter.

Quantitative Calculations in Four Component Systems. The changes which a system of known composition will experience when certain components are added to or subtracted from it may often be calculated by a combination of graphic and algebraic methods. Let it be assumed, for example, that a certain solution, represented by 30 equivalents of Na_2SO_4, 10 of K_2SO_4, 12 of $MgSO_4$ and 1000 moles of water is evaporated at 35°. Such a solution would be represented in Figure 45 by the point *p*. Evaporation will cause changes corresponding to movement away from the origin until the surface representing saturation with glaserite is reached at *q*. Further evaporation will cause movement along crystallization paths to *r* and finally to P. The exact locations of *q* and *r* are difficult to fix, but since P is known to correspond to 99.8 equivalents of Na_2SO_4, 16.6 of K_2SO_4 and 41.6 of $MgSO_4$ the substances eliminated as vapor or as solids can be calculated.

Let it be assumed that x moles of water separate as vapor, y moles of glaserite separate as solid and z moles of astracanite separate as solid, then the following equations are true:

$$(1)\quad \frac{30-y-2z}{1000-x-4z}=\frac{99.8}{1000}$$

$$(2)\quad \frac{10-3y}{1000-x-4z}=\frac{16.6}{1000}$$

$$(3)\quad \frac{12-2z}{1000-x-4z}=\frac{41.6}{1000}$$

from which x = 721, y = 1.749 and z = .208. The fact that these values are all positive indicates that the original assumption as to the crystallization paths followed was correct. The amounts of glaserite and astracanite separated might have been obtained by use of the projection diagram of Figure 45. Since p contains 57.7 per cent of Na_2SO_4, 19.2 of K_2SO_4 and 23.1 of $MgSO_4$, p' is easily located in the glaserite field of the heavy lines, and the crystallization path which passes through p' intersects P'Q' near P'. The composition of P' on the projected diagram becomes 63.16 Na_2SO_4, 10.56 K_2SO_4 and 26.3 $MgSO_4$. If y represents the equivalents of glaserite and z those of astracanite which separate in passing to P' these equations follow:

$$\frac{57.7-y-2z}{19.2-3y}=\frac{63.16}{10.56}\qquad \frac{57.7-y-2z}{23.1-2z}=\frac{63.16}{26.3}$$

Solved, y equals 3.42 and z equals .428, which values are approximately twice those obtained by the preceding calculation, because the amounts of solution used in the two calculations are related as 52 to 100. It is also possible to read from the diagram the composition of the mixture at r and to calculate the amount of glaserite which separated from p' to r' and from r' to P. Finally, by again making use of the original diagram the water which has separated after each stage of the process can be calculated.

The Jänecke Method of Representing Four-Component Systems. The water present in these systems assumes a different rôle from that of the other electrolytes and there is justification for treating it differently in the graphical representation. Jänecke refers the percentages of the three salts in the liquid phase to an equilateral triangle, and the water associated with 100 parts of the

dissolved salts to perpendiculars to the plane of the triangle. Expressed as a formula the method is: x parts of salt A, y parts of salt B, $100 - (x + y)$ parts of salt C and $100m$ parts of water, in which m represents the water associated with one part of the mixed anhydrous salts in the liquid phase. The units employed

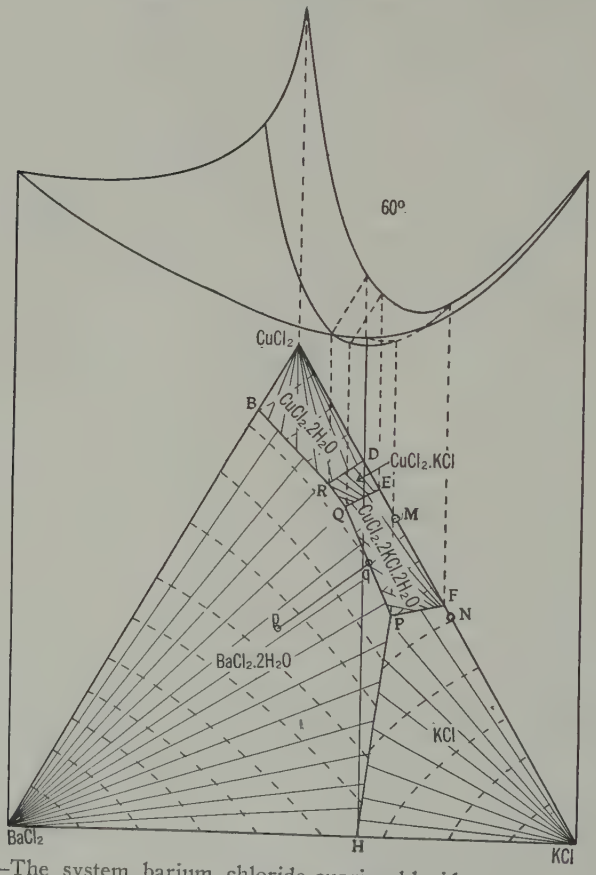

FIG. 47.—The system barium chloride-cupric chloride-potassium chloride-water represented by the Jänecke method.

may be either grams, moles or equivalents. This procedure has been employed in Figure 47 in representing the system $BaCl_2$-$CuCl_2$-KCl-H_2O, the data for which were obtained by Schreinemakers and de Baat.[4] The horizontal base gives the percentages.

[4] Schreinemakers and de Baat, *Proc. Acad. Sci.*, Amsterdam, *17*, 782 (1914).

by weight of $BaCl_2$, $CuCl_2$ and KCl in the mixture of salts which would be obtained if the solutions, saturated as to one or more of the five solids, were evaporated to dryness and the resulting residue dehydrated. The curves directly above the heavy lines of the horizontal base were obtained by joining the points representing the water associated with 100 grams of anhydrous salts. They outline a series of surfaces which separate spaces representing unsaturated from saturated solutions. It is also possible to indicate roughly a further series of curves representing solutions requiring the same amount of water for the solution of 100 grams of mixed salts. They are shown projected on the horizontal base as broken curved lines. They indicate that the solution having the lightest concentration of dissolved salts is somewhere near the RQ line.

A series of lines, representing changes in the composition of the salts in saturated solutions, resulting from evaporation at the chosen temperature of 60° which correspond to the crystallization paths of the diagram already discussed, have also been drawn on the horizontal base. The method used differs in no respect from that already used in discussing Figure 45. Since these lines are all on a projection plane the composition of points on them can be ascertained by direct measurement which is not true of the space lines of Figure 45. The general trend of the crystallization paths as drawn indicates that there is but one crystallization end point, located at R. Further, since none of the lines representing systems with two solid phases are intersected by lines joining the points representing the composition of the solids with which these solutions are saturated there are no other congruent points in the interior of the diagram. On the periphery neither M nor N is a congruent point.

A number of useful calculations can be made from the projected diagram. If an unsaturated solution which contains the three salts in the proportions represented by the point *p*, is evaporated it will first become saturated with $BaCl_2.2H_2O$ where the water per 100 grams of salt corresponds to a point directly above p in the saturation surface above the BRQPH $BaCl_2$ area of the projection. This amount of water can be estimated roughly from the curves on the projection. If evaporation is continued $BaCl_2.2H_2O$ must continue to separate and the composition of the salts in the resulting solution must change until represented by *q* at

which solid $CuCl_2.2KCl.2H_2O$ will separate. Further evaporation will cause both solids to separate until Q is reached at which point the $CuCl_2.2KCl.2H_2O$ will change to $CuCl_2.KCl$ and on further evaporation this salt and $BaCl_2.2H_2O$ will continue to separate until the crystallization end point is reached at R. Since it is possible to read directly from the diagram the proportions of salts in the solution at every stage of the process the amounts which separate from a known amount of mixture at each stage can be calculated. In a similar manner it is possible to calculate the changes which take place when a mixture of the three solid salts is treated with water.

Three Component Solid Solutions. There are only few combinations of three salts which resemble each other in both chemical and crystallographic properties sufficiently to make the formation of a continuous series of three component solids possible. Illustrations in which two of the three possible pairs of salts form double salts, which double salts form solid solutions with each other are fairly numerous. As in all cases of solid solution formation where water is also present it is associated with a simple or double salt in some definite stoichiometrical relation, and need not be considered separately. Within certain limits the systems referred to can be considered three-component systems. This is possible if the liquid phase is limited to those mixtures which can always be expressed in terms of two components by using double salts as components, but it is not possible as soon as this restriction is eliminated. An illustration is furnished by the system ammonium cupric sulfate-potassium cupric sulfate-water, investigated by Hayami,[5] represented in Figure 48. In this system $(NH_4)_2SO_4$ and K_2SO_4 form Solid Sol. I and the double salts $(NH_4)_2SO_4.CuSO_4.6H_2O$ and $K_2SO_4.CuSO_4.6H_2O$ form Solid Sol. II. These salts in addition to $CuSO_4.5H_2O$ are the only solids present at 25°. The Jänecke method has been used in representing the molal percentages of the salts present in the liquid phase. Points on the AB line represent solutions saturated as to $CuSO_4.5H_2O$ and Solid Sol. I, points on CD represent solutions saturated as to Solid Sol. I and Solid Sol. II. The point P represents the salt $(NH_4)_2SO_4.CuSO_4$ and the point Q the salt $K_2SO_4.CuSO_4$, and points on the line joining them mixtures of the two. The relations between the composition of Solid Sol. I and solutions

[5] Hayami, *Mem. Col. Sci.*, Kyoto Imp. Univ., *4*, 365 (1921).

which are saturated with it and with $CuSO_4.5H_2O$ are shown by the series of tie-lines joining points on AB and PQ. Similarly the relations between the composition of Solid Sol. I and solutions which are saturated with it and with Solid Sol. II are shown by the lines connecting points on PQ and CD. Finally, the relations between the composition of Solid Sol. II and the solutions which are saturated with it and Solid Sol. I are shown by the lines con-

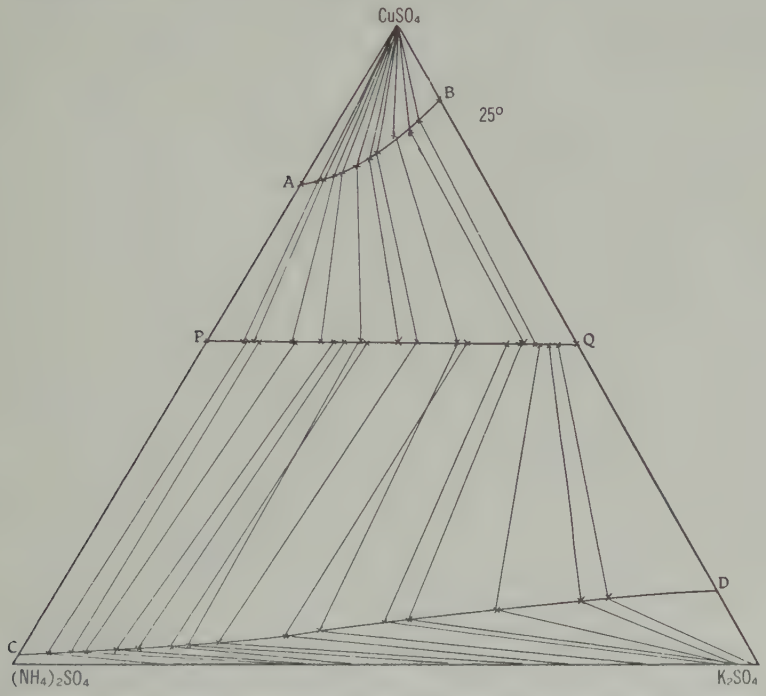

FIG. 48.—The system ammonium cupric sulfate-potassium cupric sulfate-water at 25°.

necting points on CD and the $(NH_4)_2SO_4$-K_2SO_4 side of the triangle. The diagram gives no information as to the amounts of water associated with the salts in the mixtures represented.

Effect of Temperature Upon Four-Component Systems. Varying temperature affects the systems under consideration by altering the limits of the concentrations of the solutions with which each of the solid phases can exist in equilibrium. Certain solids may be unable to exist with solutions of any concentration and

certain new solids may become stable when certain temperature changes are made. These effects are best shown by preparing a series of isothermal diagrams of the system under consideration. Such a series for the system $MgSO_4$-K_2SO_4-Na_2SO_4-H_2O was prepared by D'Ans.[6] It is reproduced in Figure 49, in which all figures are drawn to the same scale.

The striking difference between the figures for 0° and 35° is due in large measure to the substitution of Na_2SO_4 for the much less soluble $Na_2SO_4.10H_2O$, which greatly extends the limits of the 35° figure along the OA axis. In the absence of other salts Na_2SO_4 and $Na_2SO_4.10H_2O$ are in equilibrium with the saturated solution at 32.48°, but the addition of K_2SO_4 and $MgSO_4$ should increase the molal concentrations of the resulting solution and reduce its vapor pressure. This would lower the temperature needed to enable Na_2SO_4 to exist as a stable phase in contact with it. Point U of the 0° diagram represents the solution which exerts the lowest vapor pressure possible for this system at this temperature and hence Na_2SO_4 might be expected to appear first in solutions saturated with $MgSO_4.7H_2O$ and schönite. This conclusion may be incorrect owing to the appearance in the system of astracanite, which salt can exist as a stable solid in the system $MgSO_4$-Na_2SO_4-H_2O at a point corresponding to B at 20.6°. The addition of K_2SO_4 to the system should cause it to become stable in solutions saturated with $MgSO_4.7H_2O$ and schönite at a somewhat lower temperature. The lowest temperature at which Na_2SO_4 could appear might then be looked for in solutions saturated as to glaserite and astracanite. The validity of this suggestion is strengthened by the large concentrations of K_2SO_4 in solution P at 35°. It is not improbable that Na_2SO_4 appears at both of the points suggested, but that the field near the point S, within which it exists as a stable solid, begins to decrease in size and disappears entirely before 35° is attained. There is no reason why two separate Na_2SO_4 fields, separated by the astracanite field, should not appear on the diagram for a certain range of temperature.

The temperature at which Na_2SO_4-$Na_2SO_4.10H_2O$-$MgSO_4.7H_2O$-schönite and Na_2SO_4-$Na_2SO_4.10H_2O$-astracanite-glaserite exist in equilibrium with solutions of the proper composition must be fixed, and both represent invariant points.

[6] D'Ans, *Kali*, *9*, 218 (1915).

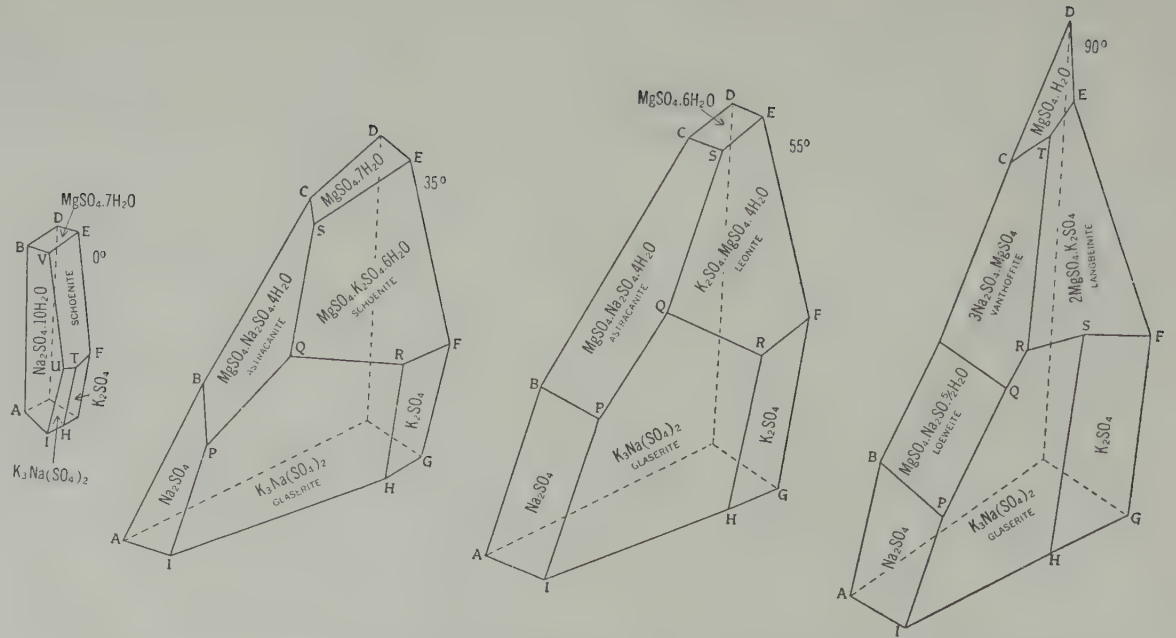

FIG. 49.—The system magnesium sulfate-potassium sulfate-sodium sulfate-water at 0°, 35°, 55° and 90°.

The greatly increased size at 35° of the K_2SO_4, $MgSO_4.7H_2O$, glaserite and schönite fields must be attributed in part to the greater solubility of all the salts concerned, but especially to the substitution of Na_2SO_4 and astracanite for $Na_2SO_4.10H_2O$. These changes are necessarily associated with changes in crystallization paths, but a somewhat surprising effect is the appearance of a new crystallization end point at Q.

In changing from the 35° to the 55° figure schönite is replaced by leonite, which change is associated with the loss of two molecules of water of crystallization. This change takes place at points corresponding to E at about 41° but at points corresponding to S it should take place at a decidedly lower temperature. A second change is the replacement of $MgSO_4.7H_2O$ by $MgSO_4.6H_2O$. In solutions of $MgSO_4$ only, this change first appears at 48°; if saturated as to both $MgSO_4.7H_2O$ and schönite it appears at 47.2°; at points corresponding to S it should appear even lower than this. Finally, it is to be noted that Q is no longer a crystallization end point, owing to the fact that there is no longer a congruent point on the QS line. Two additional invariant points with the solid phases, schönite, leonite, astracanite, $MgSO_4.7H_2O$ and leonite, astracanite, $MgSO_4.6H_2O$, $MgSO_4.7H_2O$ should be looked for between 35° and 55°.

Passing to the 90° figure it will be noted that astracanite is replaced by löweite ($MgSO_4.Na_2SO_4.5/2H_2O$) and vanthoffite ($3MgSO_4.Na_2SO_4$). Löweite first appears in equilibrium with $MgSO_4.6H_2O$ and astracanite at 61°, probably at a lower temperature when the solution contains K_2SO_4 also. Vanthoffite first appears in equilibrium with Na_2SO_4 and astracanite at 57° but the presence of K_2SO_4 evidently does not reduce its temperature of formation to 55°. A further change is the substitution of langbeinite ($3MgSO_4.K_2SO_4$) for schönite. This compound first appears in solutions saturated with $MgSO_4.6H_2O$ and leonite at 60° or with K_2SO_4 and leonite at 89°. A third change consists in the substitution of $MgSO_4.H_2O$ for $MgSO_4.6H_2O$. This takes place in solution of pure $MgSO_4$ at 67° but is reduced by the presence of K_2SO_4 and Na_2SO_4. Finally the location of one crystallization end point has changed from P at 55° to R at 90°. At least seven additional invariant systems are to be looked for in the temperature interval here considered.

Four-solid Invariant Points. In the preceding paragraph it is shown how the transition of certain three-solid systems into four-solid invariant systems can be predicted. In all of these illustrations the chemical equation representing the process at the transition point is essentially one of dehydration, which can be related to a temperature change without difficulty. If the reaction concerned does not include a hydration change other methods must be employed. It is often possible to predict the existence of such points and to ascertain roughly the values of the variables at these points by plotting in succession the concentrations of each one of the three concentration variables against the temperature for the three-solid monovariant equilibria involved. If for example the data for the polythermal line which includes Q of Figure 46 give the composition of solutions representing two systems above and two below the lowest temperature at which leonite first appears it should be possible to ascertain the values for the variables of this system by passing lines through the two sets of points until they intersect. Either method must be tested by following the course of one or both of the three-solid polythermal lines experimentally. The final proof of the accuracy of the values found can be based upon a study of the changes in the heat content or the vapor pressure or the volume of the system, just as with less complex systems. Unfortunately the rate of reaction is in many cases so slow that these methods are far from satisfactory.

Graphic Representation of Temperature Changes in Four-Component Systems. It is clearly impossible to represent the effect of temperature upon the systems here considered unless a simplifying assumption is made. The least objectionable one is to disregard variations in the water and to express variations in the relative proportions of salts by means of an equilateral triangle, and the temperature on a third axis at right angles to the plane of the triangle. This is the method of Jänecke already used in dealing with three-component systems. By recalculating the data upon which the four diagrams of Figure 49 were based, drawing the four isothermal triangles representing the system at the four temperatures at the proper distances above each other, and connecting the two- and three-solid systems in accordance with the suggestions of the preceding section a diagram is obtained which gives a fair notion of the effect of temperature upon the entire system.

A complete survey of the effect of temperature on such systems would include temperatures varying from that of the lowest cryohydrate system to that of the melting point of the salt whose melting point is highest. Complete data for such a system are not available but Figure 50 represents such a system, the variables of which have been arbitrarily chosen. It assumes that the three

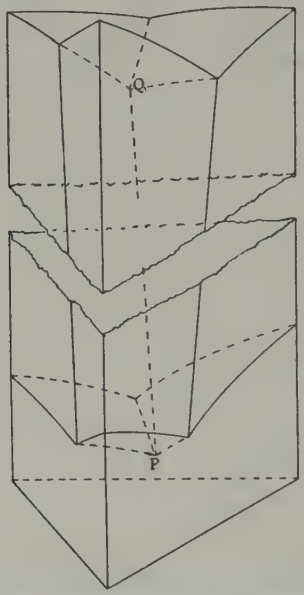

FIG. 50.—Complete temperature-composition diagram for a hypothetical four-component system.

salts, A, B and C form neither hydrates, double salts nor solid solutions, and that the solubilities of the three component salts increase continuously with increasing temperature up to the fusion point of the pure salts. In such a system the four-solid cryohydrate point at P must be connected with the three-solid eutectic point at Q by a line in space, which represents equilibrium between water and the three simple salts.

Chapter VIII.

Systems Derived from Water and Two Electrolytes Which do not Yield a Common Ion.

Reciprocal Salt Pairs. The equilibria which must exist between two electrolytes which do not yield a common ion can be expressed by the equation

$$AM + BN = AN + BM,$$

in which A and B represent acidic and M and N basic constituents. Such equilibria involve a simple interchange between the acidic and basic constituents or simple metathesis. Systems of this kind were designated by Meyerhoffer [1] "reciprocal salt-pairs," but the term is now generally applied to systems of this kind in which water is present as an additional component. In the presence of water the equilibria are determined almost entirely by the extent to which the four salts are dissociated and by the relative solubilities of these salts and their different hydrates. If the salts are capable of forming double salts or solid solutions the solubilities of these are also important factors in the equilibria.

Choice of Components. The liquid phase associated with these systems must contain at least four different ions; it may contain appreciable concentrations of a number of complex ions and of hydrogen or hydroxyl. The composition of the entire mixture can, however, be expressed in terms of the simple ions present unless affected by the separation of solids more acidic or more basic than the component salts. This may occur if one of these salts is largely hydrolyzed and if one of the resulting products is but slightly soluble. If unusual cases of this kind are disregarded the composition of the liquid phase can be expressed in terms of water and any three of the simple ions. This fact, which was first recognized by Meyerhoffer,[2] is a necessary consequence of the fact

[1] Meyerhoffer, *Sitzb. Wien. Akad., 104,* II, b, 840 (1895).
[2] Meyerhoffer, "Phasenregel," Leipzig, p. 60 (1892).

that the sum of the number of equivalents of anion must equal the sum of the number of equivalents of cation, therefore the concentration of the solution with respect to the ion not used as a component can be found by difference. With the same restriction the composition can also be expressed in terms of any three of the four salts concerned. If for example AM, BN and AN are used as components the unused salt, namely BM, can be expressed as AM + BN — AN, for there is no objection to using negative values in expressing these concentrations. Since these systems can be defined in terms of three, rather than four ions or salts, and water they are four-component systems. In practice, however, it will be found more convenient to avoid the use of negative quantities and to employ different combinations of three ions or three salts to express the composition of all possible mixtures. The simple stoichiometric relation which must exist between these ions or salts makes it desirable to express the composition of mixtures of them in terms of equivalent rather than simple weights. This involves using molal weights of salts like NaCl, half molal weights of salts like $MgSO_4$ or Na_2SO_4 and one third molal weights of salts like Na_2HPO_4. Unfortunately many investigators have used double molal weights of salts like NaCl and molal weights of salts like $MgSO_4$. Although perfectly logical this procedure differs from the conventional method of expressing equivalent concentrations in other lines of chemical work and should be abandoned.

Stable and Unstable Salt Pairs. When considered as complete systems, reciprocal salt pairs must be thought of as including four different pairs of salts each with a common ion, namely AM-AN, BM-BN, AM-BM and AN-BN. These four three-component systems form the limiting values for the more complex four-component system and are convenient starting points from which to begin the study of the latter. If all four components are concerned, invariant systems are not possible unless six different phases are present. Assuming that the system includes a liquid and a vapor phase, four solids must be present if the values of all variables, namely pressure, temperature and four concentrations are fixed. If it be assumed that the four solids are the four simple salts the liquid phase must be saturated with the four salts simultaneously, and must have a fixed concentration as to all these salts at the invariant temperature. This is not only required by the

phase rule but is a consequence of the mass law which demands that

$$C_I AM \times C_{II} BN \times K = C_{III} AN \times C_{IV} BM,$$

in which C stands for the different concentrations of the four salts in the saturated solution. These concentrations are in turn determined by the concentrations, or more correctly by the activities, of the different ions into which these salts dissociate. If the temperature is changed the two activity products no longer bear the proper relation to each other and one of the four solids must disappear leaving either AM-BN and one of the two remaining salts, or AN-BM and one of the two remaining salts. The pair which does not disappear must have the smaller activity product because the solution must be saturated with this pair of salts rather than the other. If an increase in the temperature above that of the invariant point causes the activity product of AM and BN to become less than that of AN and BM the system AM, BN and either AN or BM will result. If increasing the temperature causes AN and BM to disappear decreasing it must cause AM and BN to disappear. The two pairs of salts which exist in equilibrium with a third, one pair above and the other below the equilibrium temperature, were called "stable pairs" by van't Hoff and Reicher.[3]

Invariant Points in Reciprocal Salt Pair Systems. The invariant points of the systems under consideration represent fixed temperatures at which four solubility curves, each saturated as to three different solids, intersect. A fifth curve, representing equilibria between water vapor and four solids, and a sixth representing equilibria between a liquid and four solids, also meet the solubility curves at this point. The peculiarity which distinguishes the reaction which takes place at the invariant point is the fact that the composition of the liquid phase remains constant. In the hypothetical example cited in the preceding paragraph the composition of the liquid phase remained constant because the acidic and basic constituents of the four solids replaced each other equivalent for equivalent. In some cases the amount, but not the composition, of the liquid as well as the solid phase can change. Thus, in the system potassium chloride-sodium sulfate-water an invariant point has been found at 4.4°, at which the four solids

[3] van't Hoff and Reicher, *Z. physik. Chem., 3,* 482 (1889).

are $Na_2SO_4.10H_2O$, KCl, $K_3Na(SO_4)_2$ and NaCl. The composition of the liquid [4] in equilibrium with these solids was found to be represented by

$$1000H_2O—5.42SO_4—14.39K_2—51.83Na_4—60.8Cl_2.$$

It can be calculated from these data that the equilibrium in question should be represented by the expression:

$$2.217Na_2SO_4 \cdot 10H_2O + 3.576KCl \rightarrow 3NaCl + K_3Na(SO_4)_2 + 20.793 \text{ solution.}$$

In this reaction the water of crystallization of the Glauber's salt dissolves the four salts in such proportion as to yield a saturated solution of the composition required. The stable pair below 4.4° is $Na_2SO_4.10H_2O$ and KCl; above it the stable pair is $K_3Na(SO_4)_2$ and NaCl.

The Graphical Method of Löwenherz. Graphical representation of changes in all six of the variables concerned in these systems is not possible unless certain simplifying assumptions are made. If variations in pressure are disregarded, if the temperature is fixed, and if a constant amount of water is assumed, changes in the four remaining variables can be represented by the device first suggested by Löwenherz.[5] He represented the ratios between the number of equivalents of each of the four salts and 1000 moles of water on four axes assumed to intersect in space like the edges of a regular four-sided pyramid. Adjacent axes must be used to represent salts which contain a common ion. If this requirement is not complied with it is not possible to represent a continuous series of changes in the composition of the system. Further, since the changes may be the result of a chemical reaction it becomes necessary to express all of the concentrations involved in terms of equivalent quantities, a restriction which does not apply to the diagrams used for the simpler systems considered in the preceding chapters.

Figure 51 shows how the procedure can be employed in representing a hypothetical system in which the four component salts are the only solids, and the temperature is so chosen that two univariant but no invariant systems exist. Points A, C, E and G represent solutions containing only a single salt and saturated with it; points B, D, F and H, located on the four faces of the pyramid,

[4] Meyerhoffer and Saunders, *Z. physik. Chem., 28,* 469 (1899).
[5] Löwenherz, *Z. physik. Chem., 13,* 459 (1894).

represent solutions containing two salts with a common ion and saturated with both; points P and Q, located within the pyramid, represent solutions containing three salts and saturated with all of them. The lines connecting the points B, D, F, H, P and Q outline four surfaces which represent the composition of all possible solutions saturated as to each of the four salts. The space above these surfaces represents unsaturated solutions, that below a series of mixtures of saturated solutions and one or more solids.

The preparation of diagrams from numerical data by this

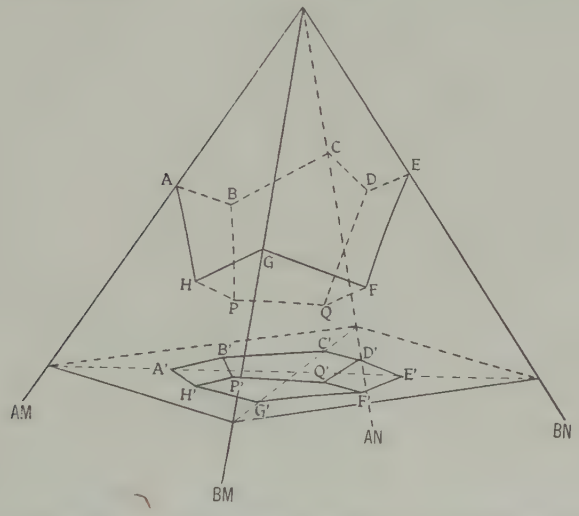

FIG. 51.—Illustrating the Löwenherz method of representing reciprocal salt pair systems.

method is time-consuming and the resulting figures may fail to indicate clearly the position and extent of the different saturation fields. These difficulties disappear if the figure is projected orthographically upon a horizontal plane. Such a projection is indicated by the lines connecting the points A′, B′, C′, D′, E′, F′, G′, H′, P′ and Q′ of Figure 51, but the system is more clearly represented where the perspective features are entirely eliminated as has been done in preparing Figure 52. In this figure the four prismatic edges form the diagonals of a square, the size of which is of no significance. These diagonals also form a pair of rectangular axes upon which the concentrations of the four salts can be laid off. The four quadrants, if considered separately, may be thought

of as representing the four three-component, common-ion containing salt systems, into which the more complex system merges as one of the three salt components is successively eliminated. The essential feature of the four diagrams is a broken line, connecting adjacent axes, and since they are projections of lines which are actually located in the four faces of the pyramid, points on them accurately represent the number of equivalents of the two salts per 1000 moles of water. The four sets of broken lines connecting these axes enclose a space within which are located points representing all the systems composed of these salts and water. It

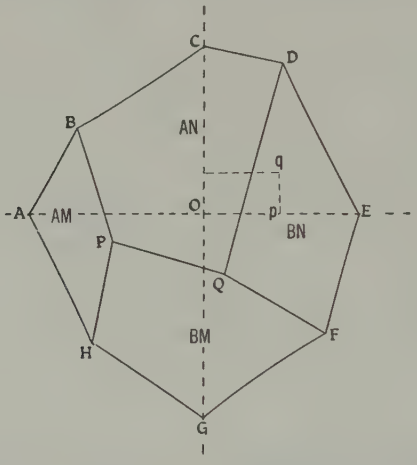

FIG. 52.—Illustrating projection of the Löwenherz diagram (Fig. 51).

should be noted, however, that all points within these lines, unlike those on the peripheral lines, represent relations and not actual amounts of the component salts. The point O for example represents pure water or any one of an infinite number of solutions in which equivalent amounts of AM and BN or of AN and BM are present. The point p represents Op units of BN plus an undefined amount of a mixture composed of equivalent quantities of BN and AM. Similarly q represents pq units of AN plus an undefined mixture of the composition p. In order to accurately define such points graphically it is necessary to erect perpendiculars to the plane which contains the axes of reference, whose lengths correspond to the total number of equivalents of electrolytes in the mixture. This last feature can usually be eliminated

because this type of diagram is usually employed for the purpose of representing relative values of the salts present only, and, when accompanied by a table giving the total number of equivalents present in each of the mixtures represented, gives a fairly satisfactory survey of the entire system at the chosen temperature.

The System Potassium Chloride-Sodium Carbonate-Water.

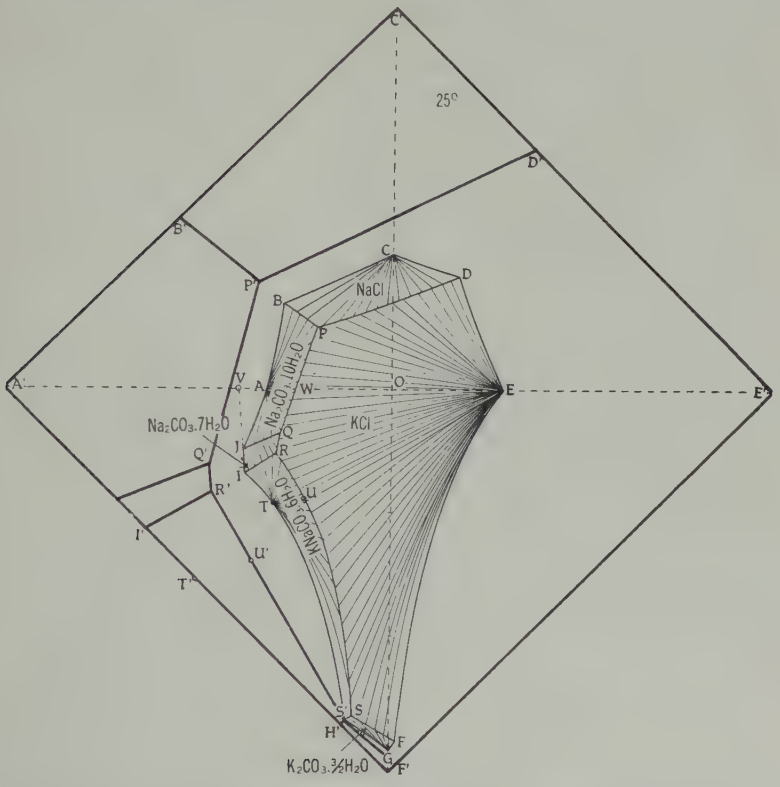

FIG. 53.—The system potassium chloride-sodium carbonate-water at 25°.

The diagram for this system which was studied by Blasdale [6] at 25° is represented by the lighter lines of Figure 53. There are six fields, each of which represents saturation as to a single solid whose composition is given by the printed label. The lines within the space surrounded by the peripheral lines represent solutions saturated as to two solids and the points P, Q, R and S solutions

[6] Blasdale, *J. Am. Chem. Soc., 45,* 2938 (1923).

saturated as to three solids, and hence univariant points. The large extent of the KCl field is a consequence of the slight solubility of that salt, and the unusual extension of the figure along the K_2CO_3 axis results from the large solubility of the solid $K_2CO_3.\frac{3}{2}H_2O$. The curvature of the lines EF, RS and IH is striking and may be correlated with the complex nature of the variations in the concentrations of the molecular species which these solutions contain.

The crystallization paths for each field must radiate from the points representing saturation as to the pure salt concerned. Those for the $Na_2CO_3.10H_2O$ field must radiate from A, those for the NaCl field from C, those for the KCl field from E and those for the $K_2CO_3.\frac{3}{2}H_2O$ field from G. Saturation as to the pure double salt $NaKCO_3.6H_2O$ must correspond to a point on the IH line and further, since we are dealing with equivalent concentrations, on a line which bisects the angle between the K_2CO_3 and Na_2CO_3 axes, that is at T. These crystallization paths must show a curvature similar to that of the IH and RS lines, but their exact form can only be ascertained by a large amount of experimental work. Saturation as to pure $Na_2CO_3.7H_2O$ is not actually attained; a large concentration of additional salts is needed to reduce the vapor pressure of the solution to a point below that at which the hepta- and deca-hydrates are in equilibrium. If it be assumed that the solubility of the heptahydrate is changed by the presence of K_2CO_3 beyond the point J at the same rate as that at which it is changed between I and J, it should be saturated with the pure heptahydrate at V and this is the point from which the crystallization paths for the field IJQR should radiate.

The location of most of the congruent points is indicated by the form of the different sets of one-solid crystallization paths. Aside from the one-solid congruent points A, C, E, G and T and the two-solid points B, D, F, H and I there are three-solid points at P, R and S. An additional congruent point saturated as to KCl and $Na_2CO_3.10H_2O$ must be located on PQ at its point of intersection with AE, namely at W. The location of still another two-solid congruent point on RS presents greater difficulties. The simplest procedure is to first prepare a clinographic projection of the figure by the method already described in discussing Figure 46 of the preceding chapter. This projection is shown by means of heavy lines; it expresses correctly the number of equivalents of the

different salts present in 150 equivalents of the mixture of salts in the saturated solution. These values could also be calculated by arithmetical methods. The resulting diagram corresponds in all essential features to the Jänecke system of graphical representation, which will be discussed in a subsequent section.

The clinographic projection of RS is R′S′; it is intersected by the line joining the points representing clinographic projections of T and E at U′. The orthographic projections of U′ must be at the intersection of RS and U′O, namely at U which represents the desired two-solid congruent point.

Of the seven two-solid congruent points B, D, F, H and I are crystallization end-points, but W and U are not. The three three-solid congruent points P, R and S are all crystallization end-points. It should be noted also that although the line JQ separates two fields it is not a crystallization path.

With these facts in mind it is easy to indicate the course of crystallization of any mixture of the salts composing the system. Quantitative calculations similar to those already outlined are also possible although necessarily somewhat more complex.

The Graphical Method of Jänecke. The Jänecke scheme for the representation of the systems discussed in Chapter VII can also be used for the representation of systems containing a reciprocal salt pair by substituting a four-sided for a three-sided prism. The relation which exists between this method of representation and that of Löwenherz has already been shown in Figure 53, but further details must be considered before it can be used intelligently.

In applying the Jänecke method to the systems described in the preceding chapters the composition of the mixtures concerned, as to the salt components, could be expressed in terms of either grams or equivalents but this is not true of the systems under consideration owing to the stoichiometrical relation which must exist between the four electrolytes if the system is classed as a four-component system. Expressed as a formula the Jänecke method is represented by

$$100m\ H_2O,\ x\ A,\ (100 - x)\ B,\ y\ M,\ (100 - y)\ N$$

in which $100m$ is the number of grams or moles of water associated with 100 equivalents of the mixture of salts present; x is the number of equivalents of one of the anions and y is the number of

equivalents of one of the cations present in 100 equivalents of that mixture. The relative proportions of the four ions in any mixture are expressed graphically by the position of a point on or within a square, the length of whose sides corresponds to 100 equivalents of salt. The method of locating such points is shown in Fig. 54. Each of the four corners of the square corresponds to a pure salt and each of the four edges to mixtures of a pair of salts containing a common ion. The corners which represent the four salts must be so chosen that these relations are complied with. Points in the interior of the square represent mixtures containing four different ions. In order to find the position of a point representing a mix-

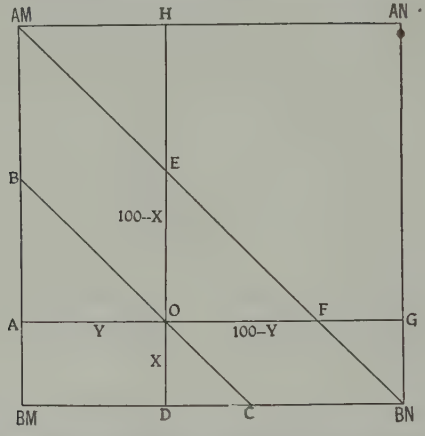

FIG. 54.—Illustrating the Jänecke method of representing reciprocal salt pair systems.

ture composed of x equivalents of A anion and y of N cation it is only necessary to measure off x units from the BM-BN line and y units from the AM-BM line, which gives the point O.

If the composition is expressed as a mixture of salts rather than of ions the location of the point in question demands more thought. The two diagonals of the square, when considered separately, can be thought of as dividing it into four right-angled isosceles triangles. The composition of all points within each of these triangles can be expressed in terms of the three salts at the apices of these triangles. Thus the point O is within the triangle outlined by AM-BM-BN and the composition of the mixture it represents can be expressed in terms of these salts; it is also within the triangle outlined by BM-BN-AN, and its composition can also be expressed in terms

of these salts but it cannot be expressed in terms of either AM-AN-BN or BM-AN-AM unless negative quantities are used. If the numbers representing the composition of the mixture are all positive quantities the salts to which these numbers belong indicate the triangle in which the point representing that mixture must be located. Having located the proper triangle it is only necessary to lay off from the point located at the right angle of this triangle distances corresponding to salts represented by the points located at the two acute angles of the triangle, and get the intersection of lines drawn through these points parallel to the sides of the square. Thus, if the composition of O is expressed in terms of AM-BN-BM it corresponds to the point found by laying off x equivalents of AM from BM, which gives the point A, and y equivalents of BN, which gives the point D, and getting the intersection of the lines AG and DH. The percentage of the third salt in the mixture must correspond to the distance of the point found from the longer side of the triangle, when measured on a line parallel to the shorter sides. Thus, the percentage of BM in the mixture represented by O equals OF or OE. This statement becomes self-evident when it is recognized that AC, DH and BC are all drawn parallel to the three sides of the triangle, and therefore that the triangles OAB, ODC and OEF are also right isosceles triangles. Hence, $100 - (x + y)$, which gives the percentage of BM, equals the distance BM-BN minus the sum of the distances BM-D and the distance D-C or the distance C-BN, which equals OF.

Use of the Jänecke Diagram. A representative diagram for a reciprocal salt pair is shown in Figure 55. It assumes that the four component salts are the only solids present and that there are two univariant points each representing systems composed of three solids, a vapor and a liquid. It is obvious that the stable pair of salts is AM and BN. Saturation as to each of the four solids corresponds to points within the four fields, and saturation as to two solids to points on the lines separating these fields. Although the diagram does not indicate the proportions of water present changes in the composition of the dissolved salts which result from evaporation of saturated solutions can be easily followed. If a solution whose composition corresponds to a point in the BN field, such as p, is evaporated that salt must separate and the resulting change in composition must correspond to movement of the point p away from the point BN until q is reached, at which

point AM also begins to separate. Further changes must correspond to movement from q away from the point representing saturation as to both AM and BN, which is on the AM-BN diagonal, namely the point R, until saturation as to a third salt is attained at Q. The points P, Q and R are congruent solutions and P and Q are crystallization end points. It will be noted that both the one-solid and the two-solid crystallization paths are straight lines, which is not true of the crystalline paths represented on the Löwenherz diagrams. It is also obvious that the changes in the composition of the dissolved salts which result when the

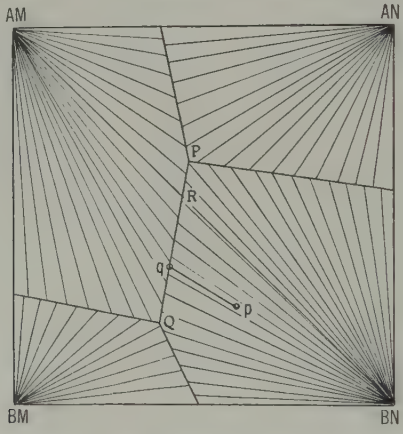

FIG. 55.—Illustrating use of the Jänecke method of representing reciprocal salt pair systems.

liquid phase is evaporated can be calculated quantitatively.

A desirable feature of the Jänecke diagram is the ease with which it may be used to express variations in the vapor pressure of the liquid phase. If the vapor pressures of a number of these solutions are determined a series of lines can be drawn on the diagram representing solutions of about equal vapor pressures from which the vapor pressures of all such solutions can be estimated roughly.

The System Magnesium Chloride-Potassium Sulfate-Water. The application of the Jänecke scheme to the graphical representation of a reciprocal salt pair system will be illustrated by the use of data obtained by Löwenherz [7] and by D'Ans [8] for the system

[7] Löwenherz, *Z. physik. Chem., 13,* 459 (1894).
[8] D'Ans, *Kali, 9,* 194 (1915).

$MgCl_2$-K_2SO_4-H_2O at 55°. The results are shown in Figure 56. The nine fields into which this diagram is divided represent the proportions of salts in the solutions saturated as to each of the nine solid phases, which can be present at this temperature. The larger fields are saturated with the less soluble solids especially K_2SO_4, KCl and the double salt, $MgSO_4.K_2SO_4.4H_2O$, which is known as leonite. A second double salt known as langbeinite, with formula $2MgSO_4.K_2SO_4$, occupies a small triangular field corresponding to mixtures containing larger proportions of

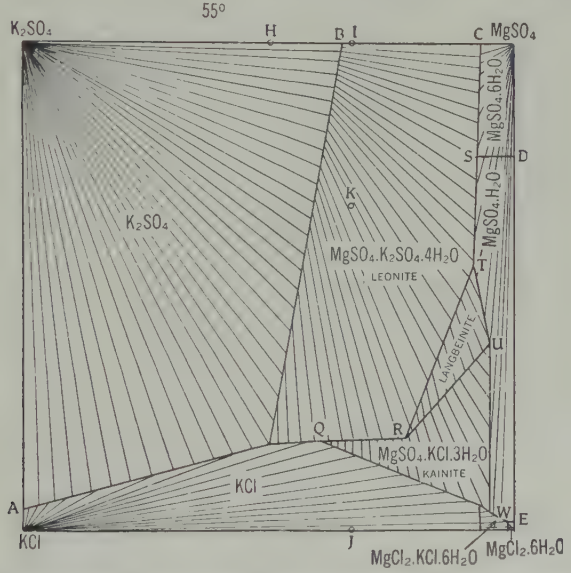

FIG. 56.—The system magnesium chloride-potassium sulfate-water at 55°.

$MgSO_4$. A third double salt, of formula $KCl.MgSO_4.3H_2O$, which is a constituent of the Stassfurt salt deposits and known as kainite, occupies a small field representing solutions containing large amounts of KCl and $MgCl_2$. It will be discussed in detail in the next section. The fields representing solutions saturated as to $MgSO_4.6H_2O$, $MgSO_4.H_2O$, $MgCl_2.6H_2O$ and $MgKCl_3.6H_2O$ (carnallite) occupy areas corresponding to large proportions of the salts from which these solids are derived.

The crystallization paths for the five simple salts radiate from the points at the four corners, which represent compositions of the

salts concerned in anhydrous form. The paths for leonite radiate from H, corresponding to $1MgSO_4 : 1K_2SO_4$; those for langbeinite from I, corresponding to $2MgSO_4 : 1K_2SO_4$; those for carnallite from J, corresponding to $1KCl : 1MgCl_2$; those for kainite from K on the KCl-$MgSO_4$ diagonal, corresponding to $1KCl : 1MgSO_4$.

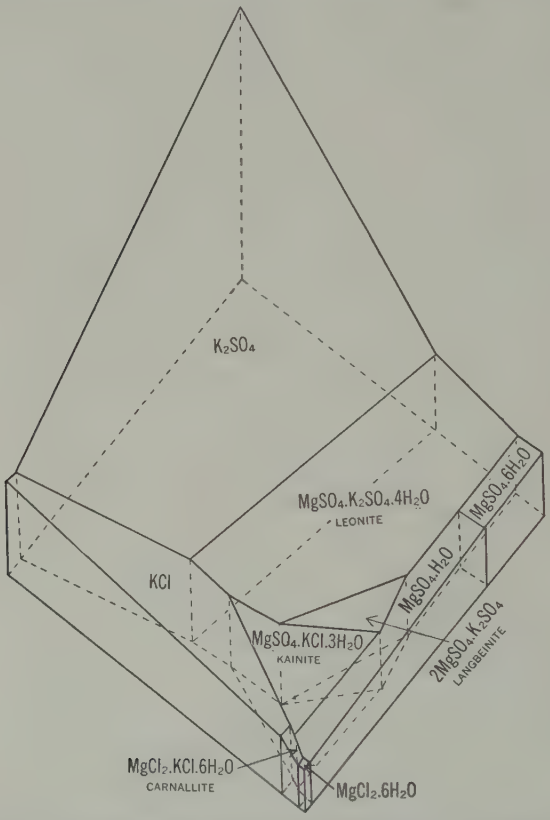

FIG. 57.—The system magnesium chloride-potassium sulfate-water showing water content of the liquid phase.

The lines separating the K_2SO_4 and leonite fields, the leonite and langbeinite fields, the leonite and kainite fields and the langbeinite and kainite fields are not crystallization paths and the only crystallization end point is at W.

By erecting perpendiculars, whose lengths are proportional to the number of equivalents of water associated with 100 equivalents of the salts corresponding to the significant points of Figure 53

and joining the ends of these perpendiculars, Figure 57 was obtained. It forms a picture of the total concentrations of the solutions saturated with the nine solids as well as of the relative proportions of the different salts in these solutions.

Tetragene Double Salts. Unlike the double salts heretofore considered kainite contains two acidic and two basic constituents. Such salts were first designated "tetragene" salts by Meyerhoffer.[9] Few salts of this type have been prepared and with the exception of kainite none of them has been studied exhaustively. Meyerhoffer showed that there are two maximum transformation temperatures above which kainite becomes unstable. These temperatures represent two different invariant systems composed of four solids, a liquid and vapor. At 85° the solids are langbeinite, kainite, $MgSO_4.H_2O$ and KCl; above this temperature the system becomes univariant by the disappearance of kainite; below this temperature it becomes univariant by the disappearance of either langbeinite, $MgSO_4.H_2O$ or KCl. At 76° the solids are carnallite, $MgSO_4.H_2O$, KCl and kainite; above this temperature the system becomes univariant by the disappearance of kainite; below this temperature it becomes univariant by the disappearance of either carnallite, $MgSO_4.H_2O$ or KCl. Attention was called by D'Ans to the fact that there are two minimum transition temperatures below which kainite becomes unstable, namely 13° and 14°. At 13° the solids are carnallite, kainite, $MgSO_4.7H_2O$ and KCl. Below this temperature the system becomes univariant through the disappearance of kainite and above it through the disappearance of either carnallite, $MgSO_4.7H_2O$ or KCl. At 14° the solids are kainite, schönite, $MgSO_4.7H_2O$ and KCl. Below this temperature the system becomes univariant through the disappearance of kainite and above it through the disappearance of either schönite, $MgSO_4.7H_2O$ or KCl. The disappearance of kainite above the two upper limits is due to the reaction

$$MgSO_4.KCl.3H_2O \rightarrow MgSO_4.H_2O + KCl + 2H_2O$$

and is essentially a dehydration process; its disappearance below the two lower limits is due to the reaction

$$MgSO_4.KCl.3H_2O + 4H_2O \rightarrow MgSO_4.7H_2O + KCl$$

and is essentially a hydration process. The temperatures which characterize the four points are largely determined by the vapor

[9] Meyerhoffer, *Z. anorg. Chem., 34,* 147 (1902).

pressures of the saturated solutions and these depend for the most part upon the concentrations of $MgCl_2$ which these solutions contain.

Reciprocal salt pair systems, which form tetragene salts, should be expected to exhibit at least two maximum and two minimum transition points at which the tetragene salt is one of the solids. This is a necessary consequence of the fact that such salts yield four different ions. The relations between the systems at the four temperatures for the ideal salt pair AM-BN, which is assumed to form neither hydrated salts nor double salts, is represented in Figure 58. It is further assumed that at the lower temperatures the stable salt pair is AN and BM and that the tetragene salt AN . BM first appears in equilibrium with AN, BM and AM at the point P. As the temperature is increased the field covered by

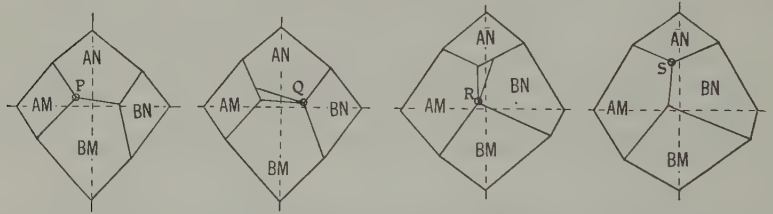

FIG. 58.—Ideal diagram showing how four invariant points are possible when a tetragene salt is formed.

the tetragene salt increases and at a certain specific temperature it can exist in equilibrium with AN, BN and BM at the point Q. It is assumed that at the upper temperatures the stable salt pair is AM and BN and at the higher of the two, the tetragene salt is in equilibrium with AM, AN and BN at the point S. As the temperature is decreased the size of the field increases until at some specific temperature it can exist in equilibrium with BN, BM and AM at the point R.

It is probable that there are but few illustrations of the formation of tetragene salts which are as simple as the one here assumed. In the formation of kainite, for example, the double salt carnallite takes the place of the simpler $MgCl_2$, and either of the double salts schönite or langbeinite takes the place of the simpler K_2SO_4. It will be noted that KCl and hydrated $MgSO_4$ constitute the stable salt pair of the transition systems for both upper and lower temperatures. Further, a more careful study of the system would

show that there are two intermediate transition points in which the double salt leonite, $MgSO_4.K_2SO_4.4H_2O$, is concerned.

Determination of Transition Points by the Method of D'Ans. A complete study of a system such as $MgCl_2$-K_2SO_4-H_2O would require the accurate determination of the temperature, partial pressure of the water vapor and composition of the liquid phase for a large number of transition points. The methods used are the same as those used for simple systems and depend upon abrupt changes in volume, in heat content, in vapor pressure of the entire system and in the composition of the liquid phase at the points in question. These methods are often difficult to use owing to the difficulty of assuring the presence of all the solids which are assumed to be present, and to the slowness with which many

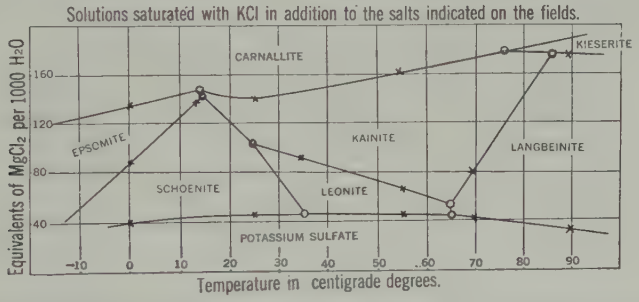

FIG. 59.—The use of graphical method in locating transition points.

such systems respond to varying conditions in the attainment of true equilibrium. Approximate values for many of the desired data can often be obtained by a study of fragmentary data already available. The use of the graphical method for this purpose, which has already been alluded to in a preceding section, will be illustrated by the work of D'Ans [10] upon the system just mentioned. His method consisted in plotting temperatures against the composition of the liquid phase as to $MgCl_2$ for points on certain polythermal lines, namely, points representing solutions saturated as to four solids, two of which were constant or differed as to hydration only. He also made use of such transition temperatures as had been experimentally determined even when the composition of the liquid phase was unknown. Figure 59 represents his work as applied to systems saturated as to KCl in addition to the solids

[10] D'Ans, *Kali*, *9*, 198 (1915).

indicated by the labels on the different fields. Points representing actual determinations of both temperature and composition are indicated by crosses and those representing estimated values by large circles. Thus the lines separating leonite and K_2SO_4 fields and the langbeinite and K_2SO_4 fields are both fixed by two crosses, and the intersection at a point corresponding to 65° and 42$MgCl_2$ gives temperature and composition of solutions as at $MgCl_2$ for the system leonite-langbeinite-K_2SO_4-KCl. Similar diagrams in which temperature was plotted against the other components of the liquid phase could have been prepared and the composition of the invariant liquid phase as to all three components fixed by a

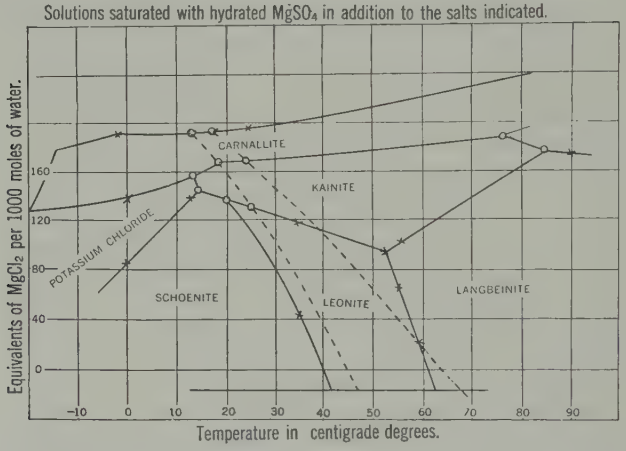

FIG. 60.—The use of a graphical method in locating the position of transition points.

similar procedure. Figure 60 is a diagram for systems saturated as to either $MgSO_4.7H_2O$, $MgSO_4.6H_2O$ or $MgSO_4.4H_2O$ in addition to the solids indicated by the labels on the different fields.

Reciprocal Salt Pairs at Varying Temperatures Represented by the Method of Löwenherz. A fair idea of the effect of varying temperature upon a reciprocal salt pair system can be obtained by constructing a series of diagrams according to the Löwenherz procedure, representing the system at a number of fixed temperatures. Such a series of diagrams for the system $MgCl_2$-K_2SO_4-H_2O at 0°, 25°, 55° and 85° is shown in Figure 61. A number of the points represented were fixed by the graphical method of D'Ans but are accurate enough to give a fairly cor-

rect idea of the changes which must take place between 0° and 85°.

At 0° there are six solids and two main two-solid crystallization paths which unite at Q and give a single crystallization end-point at S. At 25° four new solids are formed. Kainite appears at R at 13°, $MgSO_4.6H_2O$ at S at 13°, kieserite, that is $MgSO_4.H_2O$, at some unknown point at 18°, leonite at 20°.

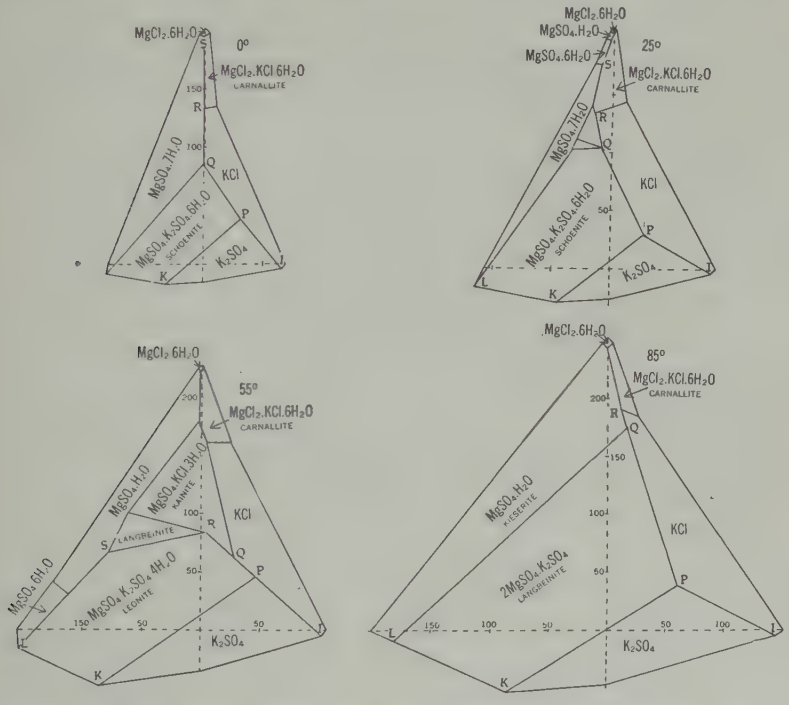

FIG. 61.—The system magnesium chloride-potassium sulfate-water at 0°, 25°, 55°, and 85°.

The fields representing saturation with these four solids attain measurable dimensions when a temperature of 25° is attained. They give rise to three additional transition points, namely, KCl-leonite-schönite-kainite at about 25°, to kainite-$MgSO_4.6H_2O$-$MgSO_4.7H_2O$-carnallite at 18° and to kainite-$MgSO_4.6H_2O$-$MgSO_4.H_2O$-carnallite at 25°. The change to 55° is associated with a broadening of the entire figure due to the increased solubility of $MgSO_4$ and KCl, the disappearance of

schönite and of $MgSO_4.7H_2O$ and of the appearance of langbeinite at 52° at the point V.

Passing to the 85° diagram it will be observed that the kainite field has disappeared, it actually vanishes at the point Q; the $MgSO_4.H_2O$ field has replaced the $MgSO_4.6H_2O$ field and langbeinite has replaced the leonite field.

In all four figures there are two main crystallization paths which unite and finally yield a single crystallization end-point at which $MgCl_2.6H_2O$ is one of the stable solids.

The effect of varying temperatures upon a reciprocal salt pair system may be represented by the Jänecke method if variations in the water content are disregarded. The procedure differs from that already used in discussing systems containing three electrolytes with a common ion in that a four-sided prism is substituted for the three-sided one. A complete representation of a reciprocal salt pair system would require data ranging from a temperature so low that no liquid phase was possible to a temperature so high that no solid phase was possible. Data for a single system of this kind are wanting but it would be easily possible to represent an ideal reciprocal salt pair system of this kind.

Metastable Equilibria in Complex Systems. It is frequently a difficult experimental task to distinguish accurately between stable and metastable systems. In preparing the data upon which Figure 53 is based it was found that in addition to the solids there noted a hydrate corresponding to the formula $Na_2CO_3.\frac{5}{2}H_2O$ frequently appeared in solutions represented by that region of the diagram which includes the points I, Q and R. It was not found possible to establish definite limits for the existence of this solid and it was finally concluded that in this system at least it was always metastable at 25°.

The rates at which equilibria are established in complex salt solutions vary greatly and are frequently very low. The slowness of such reactions may make it impracticable to use procedures which the equilibrium diagram suggests for the separation of salts present in such mixtures; it may make it possible to use successfully a process based upon the maintenance of a condition of unstable equilibrium, such as a large degree of supersaturation, for a long time interval.

Chapter IX.

Quinary or Five-Component Systems.

Systems Derived from Water and Four Electrolytes All of Which Yield a Common Ion. Mixtures composed of water and the salts AM, BM, CM and DM in which A, B, C and D represent cations and M an anion, illustrate systems of this class. If A, B, C and D represented anions and M a cation the illustration would be equally pertinent. In order to completely define such a system it is necessary to use four concentration variables, namely, the four salts or any four of the ions concerned, and in addition the total pressure and the temperature. It is difficult to obtain a clear idea of the equilibria which exist in such systems without making use of some form of pictorial representation. Even if the system is assumed to be isothermal and isobaric a four-dimensional figure would be needed to represent it graphically, and hence it becomes necessary to make use of certain simplifying assumptions. These include the following possibilities. First, the attempt to represent an entire system, that is a system composed of a liquid and one or more solid phases, may be abandoned and the composition of the liquid phase only represented. This is justifiable for, as in the simpler systems, the composition of the liquid phase fixes the composition of the other phases with which the liquid is in equilibrium. Second, it may be assumed that certain variables, such as total pressure, temperature, amount of water or total amount of salts or of any one of the salts in the solution, are constant. Third, it may be assumed that one or more of the component salts is always present in solid form and the variability of the system is correspondingly reduced. The particular simplifying assumptions which may be made use of to the best advantage depend upon the nature of the system and the purpose for which the diagram is to be used.

The System Calcium Chloride-Magnesium Chloride-Potassium Chloride-Sodium Chloride-Water. Complete data for a

single system of this class are lacking but most of the information needed for an understanding of the system containing the ions Ca^{++}, Mg^{++}, K^{+}, Na^{+} and Cl^{-} at 25° can be obtained from the work of van't Hoff, Lichenstein and D'Ans.[1] In spite of its large number of components this system includes, at least at 25°, only six solid phases. They are KCl, NaCl, $CaCl_2.6H_2O$, $MgCl_2.6H_2O$, carnallite ($KMgCl_3.6H_2O$) and tachhydrite, a double salt having the formula $CaCl_2.2MgCl_2.12H_2O$. The quinary system obviously includes four quaternary systems, namely NaCl-KCl-$MgCl_2$-H_2O, NaCl-KCl-$CaCl_2$-H_2O, NaCl-$CaCl_2$-$MgCl_2$-H_2O and KCl-$MgCl_2$-$CaCl_2$-H_2O. Data for the significant points of all but the last of these, as well as data defining the three significant points of the quinary system, are available. Several simplifications must be used in order to make graphical representation of the entire system possible. A satisfactory qualitative survey of the equilibria concerned can be attained by (1) expressing the composition of the liquid phase only, (2) disregarding the water content of the liquid phase, (3) assuming a constant amount of dissolved salts in the liquid phase, (4) assuming that pressure and temperature are constant. These restrictions reduce the number of variables to three and make it possible to represent the system by means of the regular tetrahedron already used in Figure 43 in representing systems composed of water and three salts with a common ion. It differs from the latter in that the water which has been disregarded is replaced by a fourth salt with a common ion. Each of the four faces of the tetrahedron represents one of the four quaternary systems and the space included by them the quinary system. In preparing the diagram shown in Figure 62 it has been necessary to arbitrarily assume the location of the significant points in the $CaCl_2$-$MgCl_2$-KCl plane, and to exaggerate the proportions of NaCl and KCl present in the fields and spaces representing saturation as to the remaining solids, in order to make the diagram understandable. The actual spaces representing the solid $CaCl_2.6H_2O$ if correctly drawn would be but a small fraction of that actually shown. The figure as drawn correctly represents all the equilibria possible at 25°. At the points P, Q and R four different solids are in equilibrium with solution and

[1] van't Hoff and Lichenstein, *Ber. preuss. Akad.*, p. 235 (1905); van't Hoff, *Z. anorg. Chem., 47,* 252 (1905); D'Ans, *Kali, 9,* 153 (1915).

vapor. These solids are KCl-$CaCl_2.6H_2O$-carnallite-$NaCl$, $CaCl_2.6H_2O$-carnallite-tachhydrite-$NaCl$, and $MgCl_2.6H_2O$-carnallite-tachhydrite-$NaCl$ respectively. This diagram represents an extension of the Jänecke method already employed in dealing with four-component systems. In using the diagram it should be kept in mind that each of the six spaces into which the tetrahedron is

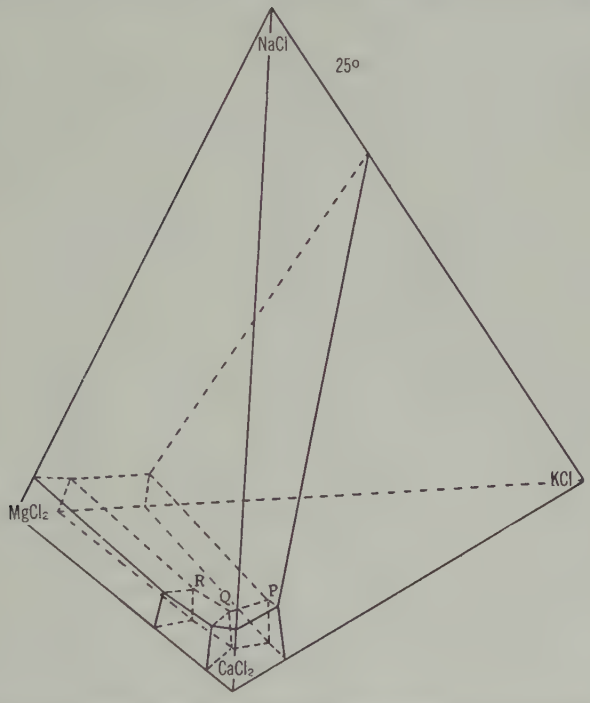

FIG. 62.—The system calcium chloride-magnesium chloride-potassium chloride-sodium chloride-water at 25°.

divided represents the range of variation in the percentages of the four salts present in 100 equivalents of the mixture of salts which the liquid phase contains.

The crystallization paths for each of the six spaces must radiate from the point representing the composition of the pure solid with which that space is saturated. The paths for the surfaces which separate these spaces must radiate from points on these surfaces corresponding to mixtures of the two solids concerned which saturate the solution in the absence of any other salts. In

order to simplify the diagram these paths are not shown on the diagram but their addition presents no especial difficulty.

Systems Derived from Water and Three Electrolytes Which Yield Five Different Ions. These systems include those with either three cations and two anions or two cations and three anions. The ions can be combined in six different ways and theoretically are capable of yielding six different simple salts in addition to a very large number of hydrates, double salts and solid solutions. They may be thought of as being made up of certain combinations of the simpler groups of salts, some of which have already been considered. If, for example, there are three cations, A, B and C, and two anions, M and N, the systems may be assumed to include

I. Two ternary systems, namely, AN-BN-CN and AM-BM-CM.

II. Three reciprocal salt pairs, namely, AN-BM, BN-CM, CN-AM.

III. Nine pairs of salts each with a common ion.

The simpler combinations form the limiting values of the complete quinary system and are convenient starting points from which to begin the discussion of it. Although there are five different ions and six simple salts concerned in such systems the total number of components needed to define them include, in addition to water, four ions or four salts.

The Stassfurt Salt Minerals. The only system of this class which has been investigated with any degree of completeness includes the ions Mg^{++}, K^+, Na^+, Cl^- and SO_4^{--} which are concerned in the formation of the most important minerals found in the Stassfurt salt deposits. The large amount of information now available regarding the system is due, for the most part, to the investigation of van't Hoff, who, with the assistance of a number of co-workers, devoted most of his life between 1897 and 1908 to this work.[2] The study of these minerals is of extreme inter-

[2] His investigations were published in the *Berichte* of the Prussian Academy of Sciences in the form of fifty-two short papers which have been reprinted under the direction of Dr. H. Precht and Dr. Ernst Cohen ("Akademische Verlagesgesellschaft," 1912) as a separate volume. Abbreviated accounts of these researches were prepared by van't Hoff and published in two volumes entitled "Zur Bildung der Ozeanischen Salzablagerung" (Viewig and Söhn [1905 and 1909]). Additional experimental data and a systematic revision of the previous work was made by

est to both chemists and geologists from a purely theoretical point of view and since they are the source of most of the potassium and magnesium salts used commercially they are of great economic importance. Although the composition of a number of these minerals has been given in the previous chapter a tabulated list of all of them will simplify the discussion which follows. The following table also includes the minerals which contain calcium and salts of boric acids, some of which will be considered in the following chapter.

Mineralogical Name	Composition
Anhydrite	$CaSO_4$
Astracanite	$MgSO_4.NaSO_4.4H_2O$
Bischofite	$MgCl_2.6H_2O$
Boracite	$MgCl_2.6H_2O.8B_2O_3$
Carnallite	$MgCl_2.KCl.6H_2O$
Epsomite	$MgSO_4.7H_2O$
Glauberite	$CaSO_4.Na_2SO_4$
Gypsum	$CaSO_4.2H_2O$
Glaserite [3]	$K_3Na(SO_4)_2$
Halite	NaCl
Hexahydrate	$MgSO_4.6H_2O$
Kainite	$MgSO_4.KCl.3H_2O$
Kieserite	$MgSO_4.H_2O$
Krugite	$4CaSO_4.MgSO_4.K_2SO_4.2H_2O$
Langbeinite	$2MgSO_4.K_2SO_4$
Leonite	$MgSO_4.K_2SO_4.4H_2O$
Löweite	$MgSO_4.Na_2SO_4.5/2H_2O$
Mirabilite	$Na_2SO_4.10H_2O$
Penta salt	$5CaSO_4.K_2SO_4.H_2O$
Polyhalite	$K_2SO_4.MgSO_4.2CaSO_4.2H_2O$
Schönite	$MgSO_4.K_2SO_4.6H_2O$
Syngenite	$CaSO_4.K_2SO_4.H_2O$
Sylvite	KCl
Tachhydrite	$CaCl_2.2MgCl_2.12H_2O$
Thenardite	Na_2SO_4
Vanthoffite	$MgSO_4.3Na_2SO_4$

D'Ans in a series of articles published in Vol. 9 of *Kali*, a technical journal devoted to the industry based upon the production and sale of potassium salts.

[3] Composition varies owing to formation of solid solutions.

The System Magnesium Chloride-Potassium Sulfate-Sodium Chloride-Water. In beginning the study of this system van't Hoff started with the reciprocal salt pair $MgCl_2$-K_2SO_4, which was discussed in the preceding chapter, and ascertained the effect upon it which resulted from the presence of an excess of NaCl. Even at constant pressure and temperature it was found necessary to make use of a simplifying assumption before the system could be represented graphically. He took advantage of the fact that since NaCl was found in all horizons in the Stassfurt beds it could be assumed that the solution from which these minerals were derived must have been saturated with NaCl. If this salt was assumed to be present as a solid phase this fact would reduce the freedom of the entire system by one degree. Furthermore, the fact that the solution was saturated as to NaCl fixed the concentration of this salt in the solution, even though this concentration had not been actually determined or was not expressed either graphically or numerically. It was also found that the addition of NaCl to the point of saturation greatly increased the concentration of SO_4 ions by interaction with K_2SO_4 and $MgSO_4$, and formed certain new solid phases, especially Na_2SO_4 and astracanite. It therefore became necessary to use Na_2SO_4 as an additional component in order to express the composition of the liquid phase. Sodium sulfate can however be expressed in terms of the salts used in representing the reciprocal salt pair itself, for Na_2SO_4 can be thought of as one of the products of the reaction,

$$K_2SO_4 + 2NaCl = Na_2SO_4 - 2KCl, \text{ and hence}$$
$$Na_2SO_4 = K_2SO_4 + 2NaCl - 2KCl.$$

Since NaCl may be disregarded, it is only necessary to reduce the KCl concentration by one equivalent, and increase the K_2SO_4 concentration by one equivalent to represent one equivalent of Na_2SO_4. The device adopted by van't Hoff for the representation of the system can therefore be reduced to the formula

$$1000H_2O,\ x\text{KCl},\ y\tfrac{1}{2}MgCl_2,\ z\tfrac{1}{2}Na_2SO_4$$

in which it is necessarily assumed that the SO_4 is combined with sodium.

Graphic Representation by the van't Hoff Method. The Löwenherz diagram for the system $MgCl_2$-K_2SO_4-H_2O may be employed in representing the more complex system under con-

sideration by introducing two changes. First, it must be recalled that the system is always saturated with NaCl in addition to the salts named on the different fields of the diagram, and the point at which the axes intersect represents a solution saturated with NaCl only. All points between this intersection and the different saturation surfaces are also saturated with NaCl, although additional salts are present in the solution. Second, it is necessary to make use of an additional axis to represent Na_2SO_4. This axis however must be midway between the negative end of the KCl axis and the positive end of the K_2SO_4 axis. It will be recalled that these axes actually represent the adjacent edges of a four-sided regular pyramid. If the added axis is projected orthographically it appears on the resulting diagram as a line bisecting the angle between the K_2SO_4 axis and the $MgSO_4$ axis, which coincides with the negative end of the KCl axis. In measuring distances along this axis it should be noted that the values used are actually being measured on the diagonal of a square and should be multiplied by $\sqrt{2}$ if measured in the same units as are used for the other axes.

The resulting diagram is shown in Figure 63. The most striking result of adding NaCl to the reciprocal salt-pair system is to narrow the entire diagram laterally, which is due to large reductions in the solubilities of KCl and the hydrates of $MgSO_4$, as compared with a negligible reduction in the solubility of $MgCl_2.6H_2O$. Many changes in the solid phases have taken place. Potassium sulfate is entirely replaced by glaserite, sodium sulfate and astracanite have replaced for the most part schönite, and the size of the kainite and leonite fields has been greatly increased. These changes are to be attributed in part to the presence of Na_2SO_4 in the liquid phase, and in part to the increased total concentration of dissolved salts, which, by reducing the vapor tension of the liquid phase in equilibrium with certain of the saturated solutions, reduces the size of the fields saturated with those hydrated salts whose vapor tensions are greatest. It is possible to read off directly from the diagram the composition of solutions represented by points on the periphery of the diagram, that is on the line A-B-C-D-E-F-G-H-I-J-K-L, but not of those solutions represented by points included within this line. The composition of solutions represented by such points

can be calculated from their location on the diagram if the total number of equivalents of salts present is known.

The crystallization paths which cross each of the saturation fields in this case represent changes in the composition of the solution associated with the separation of both NaCl and the salt in question, when evaporated at the temperature for which the

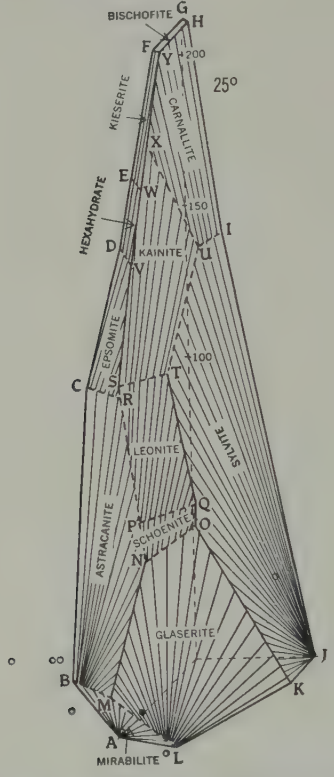

FIG. 63.—The system magnesium chloride-potassium chloride-sodium sulfate-water represented by the method of van't Hoff.

diagram was prepared. The paths for the Na_2SO_4, the $MgCl_2.6H_2O$ and the KCl fields must radiate from the points A, G and J respectively. Those for the $MgSO_4.7H_2O$, the $MgSO_4.6H_2O$ and the $MgSO_4.H_2O$ fields must radiate from the intersection of the lines CD, DE and EF respectively with the $MgSO_4$ axis. For the carnallite field they must radiate from the intersection of HI and the line representing $1KCl:1MgCl_2$; for the glaserite

field from the intersection of KL and the line representing $2K_2SO_4 : 1Na_2SO_4$; for the astracanite field from the intersection of BC and the line representing $1Na_2SO_4 : 1MgSO_4$; for the schönite field from the intersection of a line representing $1MgSO_4 : 1K_2SO_4$, which coincides with the Na_2SO_4 axis, and a line passing through a point on the PQ line to the left of P and a point on the NO line to the left of N, both of which represent solutions containing, in addition to $MgCl_2$, $MgSO_4$ and K_2SO_4 in the ratio of 1 : 1. The points can be found by either graphical or arithmetical interpolation. For the leonite field they must radiate from the point of intersection of the Na_2SO_4 axis and a line passing through a point on PQ to the left of P and a point on ST both of which represent solutions containing $1K_2SO_4 : 1MgSO_4$ in addition to $MgCl_2$; for the kainite field they must radiate from the intersection of the KCl-$MgSO_4$ axis and a line passing through a point on ST and another on UX representing solutions containing, in addition to $MgCl_2$, KCl and $MgSO_4$ in the ratio of 1 : 1. The three last-named constructions are based upon the assumption that the solubility of the solid with which the field is saturated changes uniformly when the concentration of $MgCl_2$ is reduced from the values it has at the experimentally determined points (or at points found by interpolation from such determinations) to the value it would have if that concentration became zero. The error which this assumption may involve in addition to the error of graphical interpolation introduces rather large uncertainties in the exact location of these points.

From the form and direction of these various two-solid crystallization paths it is easily possible to ascertain whether the lines separating the different fields are crystalline paths or not. It will be noted, as indicated by the use of entire rather than broken lines, that K-O-Q-T, S-V-W-X-Y, also MN, FY and HY are all three-solid crystallization paths and that Y is clearly the only crystallization end-point. The other lines, which separate saturation surfaces, indicate points at which one solid changes into another during evaporation.

Graphical Representation by the Method of Jänecke. The data used in the preparation of Figure 63 can be recalculated to correspond with the formula $100mH_2O$, xK^+, $y\frac{1}{2}Mg^{++}$, zNa^+ $100 - (x + y)\frac{1}{2}SO_4^{--}$ in which Cl^- must equal $x + y$. If NaCl

is assumed to be present as a solid its concentration for each solution has a fixed value and the Cl^- in excess of that associated with K^+ and Mg^{++} as well as the Na^+ in excess of that associated with SO_4^{--} can be disregarded. If m is also disregarded it becomes possible to represent the system by means of an equilateral triangle the three corners of which represent K^+, Mg^{++} and SO_4^{--}; or, since all the SO_4^{--} is assumed to be combined with Na^+ the three corners may be assumed to represent KCl, $MgCl_2$ and Na_2SO_4 as in Figure 64. Points in the interior of

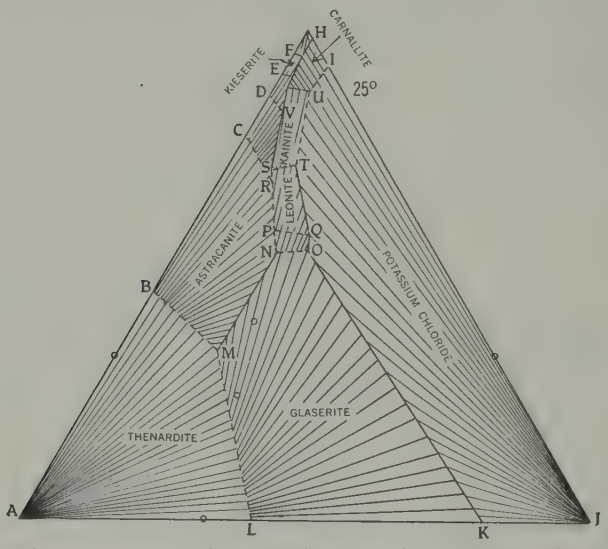

FIG. 64.—The system magnesium chloride-potassium sulfate-sodium chloride-water, represented by the method of Jänecke.

this triangle must represent solutions saturated with NaCl in addition to one, two or three of the solids named on the diagram. The number of equivalents of KCl, $MgCl_2$ and Na_2SO_4 present in 100 equivalents of the mixture of the salts, which any of these solutions contain, can be read from the location of the point on the diagram representing the solution in question. The relation between the Jänecke and van't Hoff diagrams can be easily followed if the former is thought of as a projection of the latter in an equilateral triangle whose center corresponds to the origin, and whose three apices represent solutions containing 100 equivalents of $MgCl_2$, KCl and Na_2SO_4 respectively. One

diagram may be transformed into the other by the use of methods similar to those already used in the preceding chapter.

The Jänecke diagram gives no information as to the amounts of water or of NaCl associated with the dissolved salts, although it is evident that a third axis could be added to the diagram for the purpose of expressing changes in either of these variables. It also fails to give a correct idea of the relative extents of the fields representing saturation as to the different solid phases. This will become apparent by comparing the size of the Na_2SO_4 fields of Figure 63 and Figure 64, the corresponding points of which have been given the same letters.

The crystallization paths which cross the different fields of the Jänecke diagram are all straight lines and radiate from the points representing saturation as to NaCl, in addition to the solid with which the field is saturated. These points can be located accurately by ascertaining the location of the point representing the solid in question. Thus, the point for the glaserite field corresponds to 66⅔ $\frac{1}{2}K_2SO_4$ and 33⅓ $\frac{1}{2}Na_2SO_4$; that for the kainite field to 20 KCl, 40 $\frac{1}{2}MgSO_4$ and 40 $\frac{1}{2}Na_2SO_4$. Further, the paths themselves are all straight lines and hence this diagram enables one to ascertain the crystallization paths for the entire diagram with perfect accuracy. It is often desirable to test the correctness of the crystallization paths found by use of the van't Hoff diagram by those found on a Jänecke diagram.

Graphical Representation by the Method of D'Ans. The diagram employed by D'Ans[4] combines certain of the features of the two described in the preceding sections. It agrees with the Jänecke diagram in that it reduces the concentration variables to three, namely K^+, $\frac{1}{2}Mg^{++}$ and $\frac{1}{2}SO_4^{--}$. It agrees with the van't Hoff diagram in expressing these variables as ratios between the number of equivalents of these ions and 1000 moles of water. D'Ans refers the three concentrations to three axes assumed to intersect in space at equal angles with each other but when projected on a plane surface at an angle of 120°. The complete diagram for the system under consideration at 25° is shown in Figure 65. An inspection of it shows how closely it is related to the van't Hoff figure. Its chief advantage over the latter is the greater simplicity of the process of reasoning upon which the procedure adopted in its preparation is based.

[4] D'Ans, *Kali, 9,* 234 (1915).

Representation of the Complete System Magnesium Chloride-Potassium Sulfate-Sodium Chloride-Water. All three of the diagrams described in the preceding sections represent only a portion of the entire system composed of $MgCl_2$-K_2SO_4-NaCl-

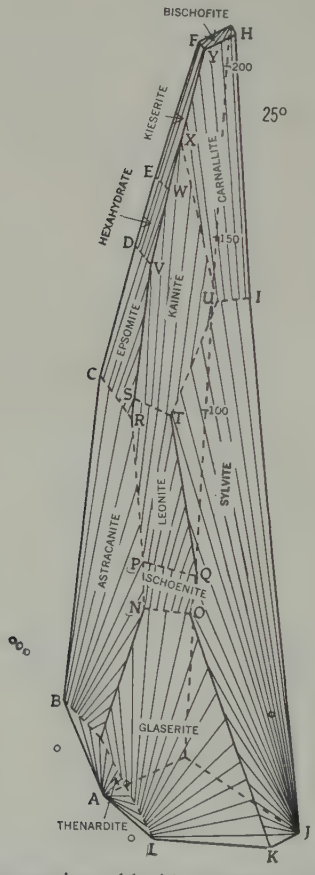

FIG. 65.—The system magnesium chloride-potassium sulfate-sodium chloride-water represented by the method of D'Ans.

H_2O, namely that portion of it which is saturated with NaCl. The addition of a fourth axis to the Jänecke diagram however makes it possible to represent the entire system. It might be suggested that the resulting figure be given the form of a regular tetrahedron, whose four apices indicate the location of points representing the four salt components, $MgCl_2$, KCl, Na_2SO_4 and

NaCl. It would be found however that these four points do not include all the space needed to express the composition of all parts of the system in question. The salts schönite and kainite for example would have to be expressed in terms of the components named by making use of negative values for NaCl as shown by the following equations:

$$MgK_2(SO_4)_2.6H_2O = 2KCl + MgCl_2 + 2Na_2SO_4 + 6H_2O - 4NaCl$$
$$KCl.MgSO_4.3H_2O = KCl + MgCl_2 + 3H_2O - 2NaCl.$$

A figure which can be used to express any possible mixture of these components is a rectangular prism, whose base is an

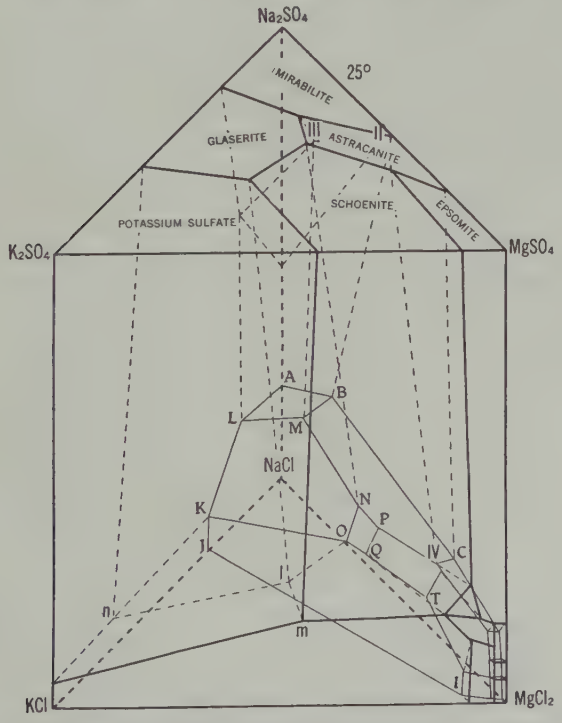

FIG. 66.—The complete system magnesium chloride-potassium sulfate-sodium chloride-water at 25°.

equilateral triangle, as first suggested by Jänecke.[5] By employing the six corners of such a figure to represent the six possible

[5] Jänecke, *Z. anorg. Chem.*, *53*, 323 (1907).

single salts a perfectly satisfactory diagram is obtained if the salts are arranged as shown in Figure 66. The nine edges of the figure have all been given the same length; they all represent a pair of salts with a common ion. The two end faces represent systems composed of three salts with a common ion, and the three faces reciprocal salt pairs. Any point within the space outlined by the figure must represent a quinary system the water content of which has been disregarded. In order to use the diagram to express the results of the work of van't Hoff at 25° it is first necessary to recalculate the number of equivalents of the different salts, including NaCl, which total 100 equivalents of mixture in the various saturated solutions. The points representing these mixtures have been located and properly connected in the diagram by a series of fine lines; they outline a solid figure included within the lower right hand portion of the prism, which bears a striking resemblance to Figure 63, although it represents a very different series of relations from those of that figure. The former expresses variation in the NaCl content of the dissolved salts in place of variations in the water content of the solution shown by the latter. The thirteen saturation surfaces outlined by the fine lines limit that portion of the prism which represents saturation with NaCl; each of these surfaces also forms one of the areas limiting that portion of the prism representing saturation as to some one of the thirteen solids of the van't Hoff diagram. An inspection of the diagrams for the quaternary systems $MgSO_4$-K_2SO_4-Na_2SO_4 and $MgSO_4$-KCl, which are represented by the heavy lines of the upper end and front face of the prism respectively, shows that two other solids, namely K_2SO_4 and $Na_2SO_4.10H_2O$ are also concerned in the quinary system. To complete the diagram for the latter therefore it becomes necessary to divide that portion of the prism which represents solutions not saturated as to NaCl into fifteen spaces, each representing saturation as to one of the solids. In order to indicate the limits of these fifteen spaces it is necessary to fix four other points, namely those representing solutions saturated with (I) potassium sulfate-potassium chloride-schönite-glaserite, (II) mirabilite-thenardite-astracanite, (III) mirabilite-thenardite-astracanite-glaserite, (IV) schönite-leonite-astracanite-epsomite. In the absence of actual experimental data the location of these points has been estimated from the location of the known points with

which they are related. They have been connected with those already fixed by means of dotted lines, in such a manner as to define the limits of the fifteen spaces representing all the mix-

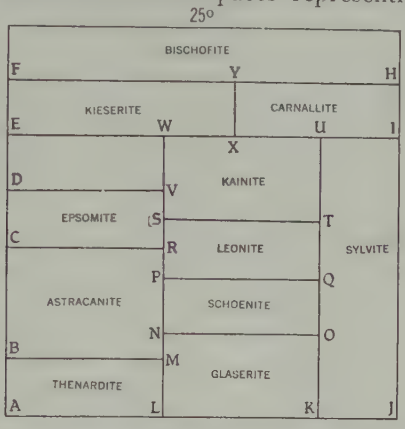

FIG. 67.—The paragenesis of the Stassfurt salt minerals at 25°.

tures saturated with respect to the fifteen solids. It was found necessary to shift slightly the position of some of the points at the lower right hand corner of the diagram in order to show

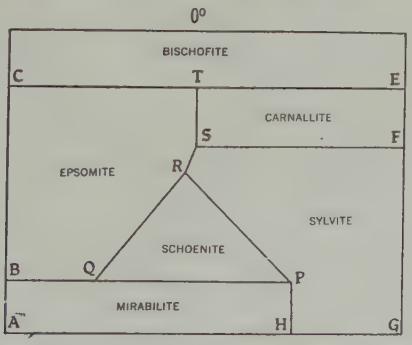

FIG. 68.—Paragenesis of the Stassfurt salt minerals at 0°.

properly the limits of the spaces which occupy this part of the prism.

Paragenesis of the Stassfurt Salt Minerals. All of the important qualitative features of the data summarized by either Figures 63, 64 or 65 can be expressed in a simpler form as in Figure 67. This diagram shows all possible combinations of

the twelve salts here concerned which can exist in equilibrium with saturated solutions of fixed composition, or, expressed more

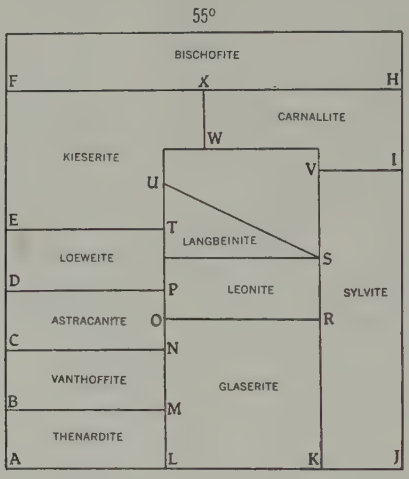

FIG. 69.—Paragenesis of the Stassfurt salt minerals at 55°.

briefly, this diagram exhibits their paragenesis, a term first used by van't Hoff. Similar diagrams, based upon data obtained or

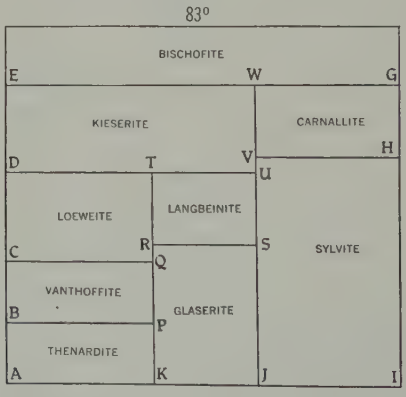

FIG. 70.—Paragenesis of Stassfurt salt minerals at 83°.

compiled by D'Ans,[6] exhibiting their paragenesis at 0°, 55° and 83° are shown in Figures 68, 69 and 70. It is easily possible to predict the successive equilibrium changes which the system

[6] D'Ans, *Kali*, *9*, 236 (1915).

must undergo as the temperature changes from 0° to 83° from a study of these diagrams. The change from 0 to 25° is marked by the appearance of six new solids, namely glaserite, astracanite, kainite, thenardite, hexahydrate and kieserite, and also by a large number of new paragenetic combinations.

Glaserite obviously results from the reaction represented by mirabilite + sylvite = glaserite + halite + solution. This reaction should take place in solutions corresponding to points on a line represented roughly by HP of Figure 68. Since the reaction involves dehydration it might be expected to take place at a lower temperature nearer P than H because the former should have a lower vapor pressure than the latter. It has been shown to take place in the presence of schönite (and NaCl) at 3° and in its absence at 4.4°.

Similarly astracanite should result from the reaction

epsomite + mirabilite = astracanite + solution

and this reaction should take place in solutions corresponding to points on a line represented roughly by RQ. It has been found to take place in the presence of schönite at 4.5° and in its absence at 5°.

Similarly kainite should result from the reaction

epsomite + sylvine = kainite + solution

in solutions corresponding to points on a line represented roughly by RS. It has been found to take place in the presence of carnallite (and NaCl) at 12°, and in the presence of schönite (and NaCl) at 12.5°. In like manner hexahydrate has been found to result from the dehydration of epsomite in the presence of bischofite and carnallite (and NaCl) at 12.5°, kieserite from the dehydration of hexahydrate in the presence of bischofite and carnallite (and NaCl) at 12.5° and thenardite from the dehydration of mirabilite in the presence of glaserite and astracanite at 13.5°.

It should be noted that all the reactions here concerned could be expressed by quantitative equations if the composition of the saturated solution involved was known. Similar predictions as to the appearance of new solids and new paragenetic combinations could be made for the 25°-55° and 55°-83° temperature interval.

Invariant Points in the Quinary System. In a quinary system which is capable of yielding as many solid phases as the one under consideration the number of possible invariant points, that is points at which five solids are present, becomes large. An accurate determination of the temperature and concentration values associated with these points is of both theoretical and practical importance. Some of these represent the maximum or minimum temperature limits for the formation of certain solid phases, others points at which the paragenesis changes. The task of ascertaining accurately the values of the variables associated with these points is a time consuming one and but few of the necessary data have been obtained. It was shown by Jänecke[7] how complete data for all these points could be obtained by a method of graphical interpolation using the following procedure based upon a new type of diagram.

The four triaxial diagrams similar to Figure 64 were superimposed on a vertical axis at intervals corresponding to the temperature interval concerned, thus forming a rectangular prism with a triangular base whose lateral faces represented temperature-concentration diagrams for the systems K^+-Mg^{++}-NaCl in excess, Mg^{++}-SO_4^{--}-NaCl in excess and SO_4^{--}-K^+-NaCl in excess. The twelve quaternary invariant points, which had been determined by van't Hoff and his associates were then located on these side faces and properly connected as shown in Figure 71, in which the three faces have been placed in their proper order but in the same plane.

A study of diagrams 67-70 indicates that there should be thirty-three different quinary invariant systems represented by points within the space enclosed by the three side faces. Each of these points must be located at the intersection of two or more lines, each line representing an invariant quinary system; the solids associated with all of these systems must be the same as those associated with the invariant point in question. Some of these lines connect known points on the four triaxial planes corresponding to the four temperatures, some are connected with the twelve invariant quaternary points on the side faces. By projecting the known lines successively upon these faces the points of intersection corresponding to the invariant quinary system can be found. It then becomes possible to ascertain the tempera-

[7] Jänecke, *Z. anorg. Chem.*, *100*, 201 (1917); *102*, 41 (1918); *103*, 1 (1918).

ture and either the Mg^{++} or K^+ or SO_4^{--} content of the liquid phase according to the face concerned. Since the data for the third component of the solution can be obtained from those for the other two it becomes possible to check some of the figures found. It is evident however that the possible error of this procedure is large. The temperatures of a number of these invariant points were determined experimentally by van't Hoff and were found to be in fair agreement with the values found by the Jänecke method. By the use of a similar procedure Jänecke was also able to determine the water content and the sodium chloride content of the liquid phase associated with each of the thirty-three points.

The diagram representing the result of Jänecke's work for the system between 25° and 55° has been reproduced in Figure 72, but the construction lines have been omitted. It will be noted that there are four quaternary points, numbered 7, 8, 9 and 10, all on the $MgSO_4$ face and that each of these is connected with a quinary point at which an additional solid containing potassium is present. Starting at 10 for example (thenardite-astracanite-vanthoffite-NaCl) and adding potassium to the system causes glaserite to appear at 11. Similarly, starting at 9 (astracanite-löweite-kieserite-NaCl) langbeinite appears at 12; starting at 7 (epsomite-astracanite-hexahydrate-NaCl) leonite appears at 17; starting at 8 (astracanite-kieserite-hexahydrate-NaCl) leonite appears at 15. Of the remaining quinary invariant points 14 marks the first appearance of langbeinite at 47°, 19 the disappearance of schönite at 26° and 20 its disappearance at 25½°. The remaining points, namely 10, 13, 16 and 18, are points at which there is a change in paragenesis.

Diagrams similar to Figure 72 for the temperature interval 0°-25°, 55°-85° and 83°-110° were also prepared by Jänecke but they do not present features which differ essentially from those already considered.

The manner in which the system which exists at any one of the invariant points is affected by varying temperature is easily predicted. At the point 11 for example the equilibrium can be expressed by the reaction

$$461.2 \text{ thenardite} + 7.266 \text{ glaserite} + 250 \text{ astracanite} + 111.4NaCl = 240.2 \text{ vanthoffite} + (1000H_2O + 9.8Mg^{++} + 21.8K^+ + 100Na^+ + 15SO_4^{--} + 111.4Cl^-),$$

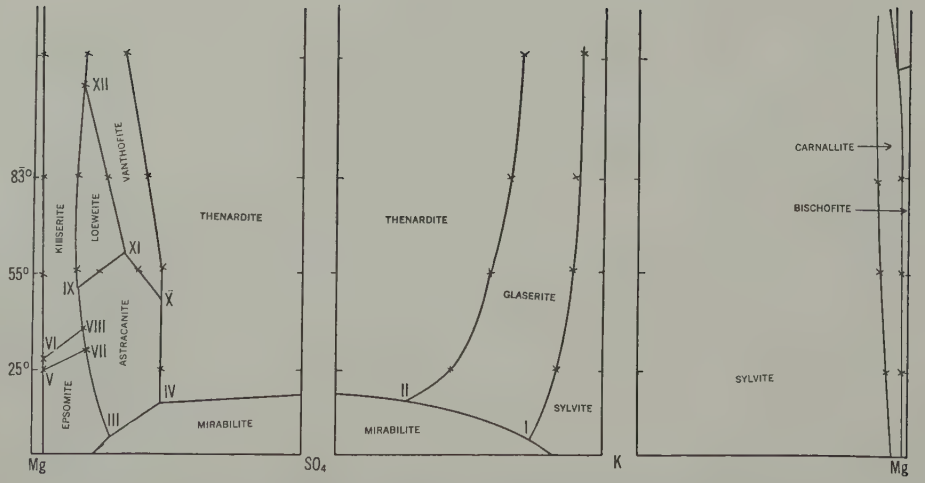

FIG. 71.—Showing effect of temperature upon the systems $MgSO_4$-NaCl-H_2O, K_2SO_4-NaCl-H_2O, and $MgCl_2$-KCl-NaCl-H_2O.

in which the composition of the liquid phase is represented by the substances in the parenthesis. Since the formation of a liquid phase can be assumed to involve the absorption of heat increas-

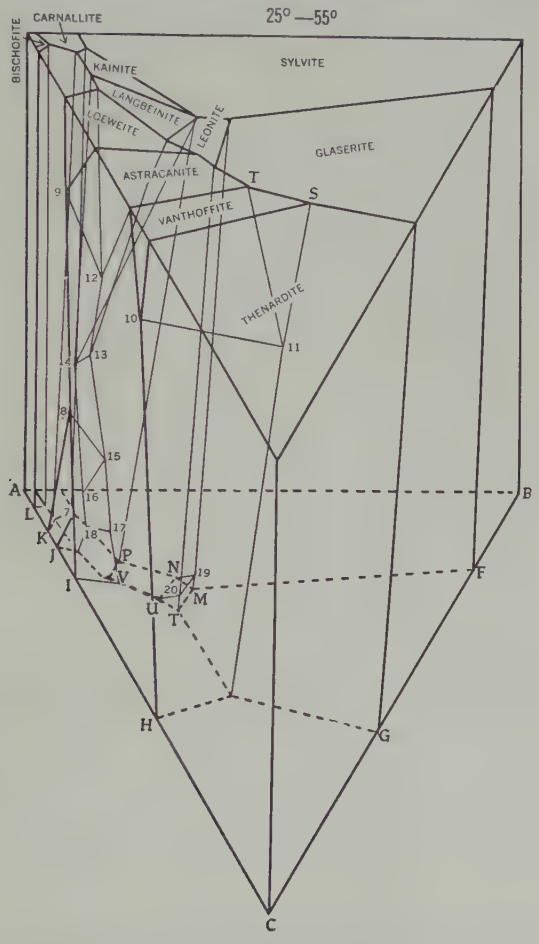

FIG. 72.—The system magnesium chloride-potassium sulfate-sodium chloride-water between 25° and 55°.

ing the temperature should cause the reaction to progress from left to right. If heat is supplied in sufficient amount the reaction will progress until one or more of the reacting solids is used up. The absence of any one of these solids yields a univariant system, and it is then possible to vary the temperature. Three of

the resulting univariant systems, namely glaserite-thenardite-vanthoffite-NaCl (line 11-S), glaserite-vanthoffite-astracanite-NaCl (line 11-T), and thenardite-vanthoffite-astracanite-NaCl (line 11-X) exist above the invariant temperature. One, thenardite-glaserite-astracanite-NaCl, exists below it. There are three other univariant systems possible; one of these includes all the solids except NaCl, hence cannot be represented on the diagram; a second includes all the solids and a vapor in place of a liquid phase; the third includes all the solids and a liquid but no vapor phase.

Chapter X.

Six Component Systems.

General Features. Six-component systems include those composed of water and electrolytes yielding six different ions, in which the number of different cations or anions may vary between one and five. It is obvious that at least eight variables must be considered in dealing with such systems and their treatment presents many difficulties unless a number of simplifying assumptions are made. Only fragmentary data relating to the equilibria which exist in a very few systems of this class are available. The composition of a series of solutions, containing an acid and a neutral salt, which are in equilibrium with a single solid, namely a slightly soluble salt of calcium, was determined by Henderson and Taylor [1] but their data do not necessitate employment of the principles of the phase theory. The information relating to certain minerals of the Stassfurt Salt deposits, obtained by van't Hoff and D'Ans, and not heretofore considered, is more comprehensive and can scarcely be understood without the use of a phase-rule diagram.

The Calcium-containing Minerals of the Stassfurt Salt Deposits. In discussing the Stassfurt salt deposits in the preceding chapter the occurrence of calcium-containing minerals, and the presence of calcium ion in the liquid phase, was disregarded although minerals which contain calcium are found in small amounts throughout the entire series of deposits, and the calcium content of the liquid phase may be large. These minerals include in addition to a large number of single and double sulfates, tachhydrite ($CaCl_2.2MgCl_2.12H_2O$) and boracite ($MgCl_2.8B_2O_3.6H_2O$). Both of these are fairly soluble compounds and are found only in the carnallite zone, that is in strata resulting from the crystallization of solutions whose composition approaches that of the solutions of sea water at the crystallization end-point. Since such

[1] Henderson and Taylor, *J. Phys. Chem.*, *20*, 672 (1916).

solutions contain very little SO_4 ion the conditions for the separation of tachhydrite are expressed with a fair degree of accuracy by the diagram of Figure 62 representing the five-component system $CaCl_2$-$MgCl_2$-KCl-NaCl-H_2O. Data relating to the formation of boracite are entirely lacking and the concentration of the solution with respect to borate ion from which boracite separates must be small.

The conditions which determine the separation of the single and double sulfate of calcium are most easily understood by considering the effect of adding calcium ion to the system $MgCl_2$-KCl-Na_2SO_4-H_2O. Introducing calcium into this system increases its degree of freedom by one, but the presence of an additional solid containing calcium decreases it by the same amount. Further, since these calcium containing sulfates are but slightly soluble the composition of the liquid phase, which is in equilibrium with the more soluble salts, should not be greatly affected by the presence of the additional solid, unless both calcium and chlorine are added to the solution as the result of interaction between a solid chloride and the solid calcium-containing salt.

Diagrams for Calcium-containing Minerals of the Stassfurt Deposits. The last statements of the preceding paragraph make it obvious that it should be possible to represent the data for the calcium-containing systems of the Stassfurt deposits by use of the diagrams already used for the calcium-free system. It is only necessary to divide the space limited by the planes of these diagrams into a number of smaller spaces, each of which represents a solution saturated as to some one solid containing calcium in addition to halite, in order to represent the equilibria in calcium-containing systems. The starting point in the preparation of such diagrams is the determination of the location of points on the edges of the simple diagrams, such as Figure 73, at which there is a liquid phase in equilibrium with two calcium-containing compounds. If the surfaces separating the spaces representing the different calcium-containing compounds intersect within the diagram, at least some of the points corresponding to these intersections must also be fixed before the separating surfaces can be properly located.

For the zero degree diagram not more than five calcium-containing solids, namely gypsum, anhydrite, syngenite, polyhalite and penta-salt, are concerned. The transition temperature for

the gypsum-anhydrite equilibrium is 65° in the absence of other salts, 30° in the presence of solid halite and below 0° in the presence of solid bischofite. Hence that portion of the diagram within which gypsum is the stable solid should include much of the space surrounding the lower portion of the magnesium

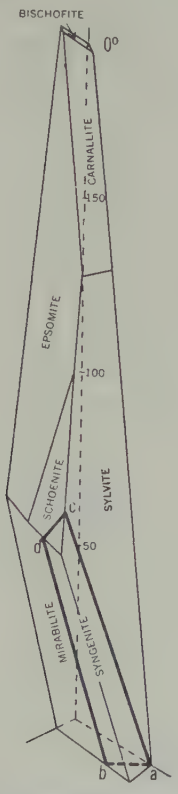

FIG. 73.—The system calcium chloride-magnesium sulfate-potassium chloride-sodium chloride-water at 0°.

chloride axis; that within which anhydrite is stable, the space surrounding the upper portion of this axis. Syngenite, $CaSO_4.K_2SO_4.H_2O$, is known to form from gypsum and solutions containing moderate concentrations of potassium salts, even much below 0°, and hence this mineral should constitute the calcium-containing solid in the space at the front of the diagram. Glauberite is formed from gypsum and mirabilite at 29° in the

absence of other salts, at 14.8° in the presence of halite, at 13° in the presence of glaserite, and at 12° in the presence of astracanite. It is not probable therefore that it occurs as a stable phase at 0°. The penta-salt, $Ca_5K_2(SO_4)_6.H_2O$, is formed from syngenite and gypsum in the absence of other salts at 31.8° and in the presence of halite at 22°, and should be looked for within the space represented by the upper part of the diagram. Three points, which fix the limits of the spaces saturated as to gypsum and syngenite, were determined by D'Ans (*l. c.*, page 262). In the diagram shown in Figure 73 they are located at *a*, at which halite and sylvite are also present; at *b*, at which halite and mirabilite are also present; and at *c*, at which schönite, halite and sylvite are present. A fourth point has been arbitrarily assumed to be located at *d*, at which schönite and mirabilite are present. That portion of the diagram in front of the *a-b-c-d* plane represents approximately the composition of all solutions saturated at 0° as to syngenite. Most of the lower portion of the diagram back of this space can be assumed to be saturated with gypsum, but it is probable that some of the upper portion of this space is saturated as to anhydrite or penta-salt or possibly as to polyhalite.

The data for the 25° diagram, shown in Figure 74, are more complete. At this temperature gypsum is entirely replaced by anhydrite, and glauberite occupies a space extending along the SO_4 axis. The point *a* indicates the composition of a solution saturated as to three calcium-containing solids, namely anhydrite, syngenite and glauberite in addition to halite. The syngenite space is limited by the planes *a-o-q-h*, *a-o-b-g-e* and *o-b-u-p-q*. The glauberite space is limited by *a-o-b-g-e* and *a-o-b-f-c*. The polyhalite space is limited by *o-r-v-j-i-q*, *o-b-p-q* and *o-b-r*. The remaining space is saturated as to anhydrite. There is also a small space extending along the plane separating syngenite from anhydrite which is saturated as to penta-salt but data relating to it are not available.

At 55° the presence of a calcium-containing solid affects the entire diagram, for at this temperature certain of these salts react with sylvite forming calcium chloride and potassium sulfate, and it becomes necessary to consider the calcium content of the solution in expressing the equilibria concerned. In accordance with the suggestion of D'Ans (*l. c.*, page 263) representation

of the calcium content of the solution is made possible by assuming that a second regular tetrahedron, representing the system KCl-$MgCl_2$-$CaCl_2$-H_2O plus solid NaCl is so located with respect to the tetrahedron representing $MgSO_4$-KCl-H_2O plus solid

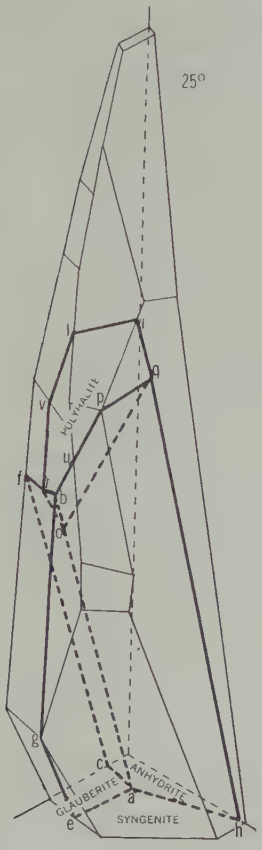

FIG. 74.—The system calcium chloride-magnesium sulfate-potassium chloride-sodium chloride-water at 25°.

NaCl, that the point representing saturation as to NaCl and the edges representing KCl and $MgCl_2$ coincide. Obviously concentrations of $CaCl_2$ would be expressed by means of an axis which coincides with that used for SO_4, but measurements expressing concentrations of $CaCl_2$ should be made in a direction opposite to that used for SO_4. If the orientation of the combined

figure is made the same as that already used for the single tetrahedron representing SO_4-$MgCl_2$-KCl-H_2O the orthographic projection of the added tetrahedron will show distortion. Concentrations of KCl and $MgCl_2$ for both tetrahedrons are expressed on the orthographic projection in terms of units which are 0.577 (0.5 divided by cos 30°) times the actual length of the edge of the reference tetrahedron. Concentrations of $CaCl_2$ however should be expressed in terms of units which are 0.963 (cos 15° 45′) times the same length, or more simply, the unit of measurement for $CaCl_2$ concentrations should be 1.724 times that for either $MgCl_2$ or KCl or SO_4. The actual data available concern solutions containing little or no magnesium and hence Figure 75,

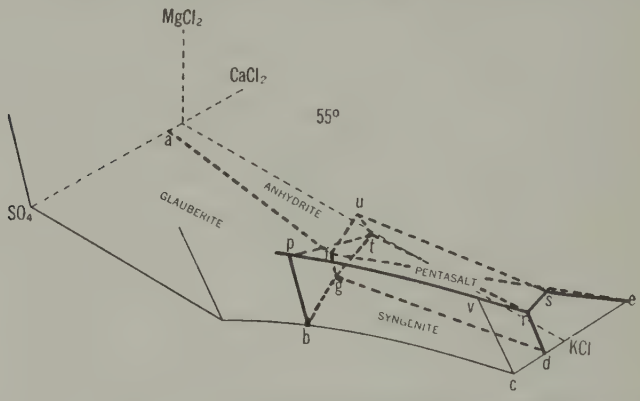

FIG. 75.—The system calcium chloride-magnesium sulfate-potassium chloride-sodium chloride-water at 55°.

which represents them, shows little more than the limits of the fields saturated as to the different calcium-containing solids for the system SO_4-KCl-$CaCl_2$-H_2O plus solid NaCl. There are four of these salts. On the base of the diagram the points *a-f-g-b* limit the glauberite field, *b-g-d-c* the syngenite field, *d-g-f-e* the penta-salt field and *e-f-a* the anhydrite field. The space representing solutions saturated as to syngenite extends from the base to the polyhalite field, from which it is separated by a surface outlined roughly by the points *r-t-p-v*. The space representing saturation as to the penta-salt extends from the base to a surface outlined by the points *r-s-u-t* at which polyhalite is the stable solid.

Similar data for the 83° diagram are available and the corresponding diagram can be prepared. It is greatly extended in the

direction of the *d-e* line of Figure 75 corresponding to larger concentrations of $CaCl_2$ than in the 55° diagram.

Calculation of Changes During Evaporation of Sea Water. Analysis of samples of sea water from different oceanic bodies have shown some variations as to the total content of dissolved salts, but remarkable uniformity as to the relative amounts of the principal salt-forming ions, namely Na^+, K^+, Mg^{++}, Cl^- and SO_4^{--}. Data regarding the less important ions, namely Ca^{++}, Br^- and BO_2^- are less conclusive but the percentages of these constituents are too small to have any significant effect upon the results obtained when sea water is evaporated. The series of changes which result when the evaporation is carried on at 0°, 25°, 55° and 83° can be readily ascertained from a study of the diagrams representing the quaternary system in question at these temperatures if the composition of sea water, which has been evaporated to the point of saturation with NaCl is known. The composition of the solution expressed in round numbers, resulting from evaporation at 25° to this point was found by van't Hoff to be expressed by:

$$1000\ H_2O - 94\ NaCl - 2\ KCl - 14.6\ \tfrac{1}{2}Mg - 7.20\ \tfrac{1}{2}SO_4.$$

These figures can also be assumed to represent the composition of the solution when evaporated at the other temperatures named, owing to the slight effect of temperature upon the solubility of NaCl.

The method of calculating the further changes resulting from the evaporation of such a solution will be followed when the temperature chosen is 0°. The diagram for the system at this temperature is given in Figure 76. The point representing the composition of the solution fixed by the work of van't Hoff corresponds to *a*, which, since it represents a solution saturated as to NaCl only, is found within the space limited by the surfaces representing saturation as to the six solids which can be formed at this temperature, namely $Na_2SO_4.10H_2O$, $MgSO_4.7H_2O$, KCl, $MgCl_2.6H_2O$, $MgKCl_3.6H_2O$ and $MgSO_4.K_2SO_4.6H_2O$. Upon evaporation NaCl must separate and the change in the composition of the solution must correspond to movement of the point *a* away from the origin until the resulting line intersects some one of the saturation surfaces. By comparing the direction assumed by this line with the limits of the surface rep-

resenting solutions saturated as to $MgSO_4.7H_2O$ it seems probable that the solid named will be the next one to separate. The correctness of the assumption, and the location of the point at which the separation begins, can be ascertained by a series of calculations, which are based upon the assumption that the sur-

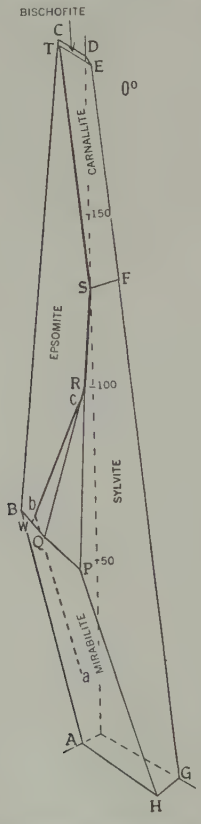

Fig. 76.—Illustrating the changes resulting from the evaporation of sea water at 0°.

face in question represents a perfect plane. If *b* represents the point at which $MgSO_4.7H_2O$ begins to precipitate the separation of further amounts of this solid must correspond to movement of *b* away from the point representing saturation as to pure $MgSO_4.7H_2O$, that is along some one of the two-solid crystallization paths of this surface, until a point on the QR line,

which will be designated as *c*, is reached. Continuing the process both $MgSO_4.7H_2O$ and schönite must separate and further changes in the composition of the solution correspond to movement of *c* to R. The composition of the solution, which is being evaporated, at the point *b* can be calculated by interpolation between the composition of solutions B, Q and R, whose values are as follows:

B = $1000H_2O$ — 48.2NaCl — 0KCl — 53.8 $\frac{1}{2}MgCl_2$ — 23.4 $\frac{1}{2}MgSO_4$

Q = $1000H_2O$ — 44NaCl — 15KCl — 48.6 $\frac{1}{2}MgCl_2$ — 31 $\frac{1}{2}MgSO_4$

R = $1000H_2O$ — 14.8NaCl — 12.4KCl — 100.2 $\frac{1}{2}MgCl_2$ — 14.8 $\frac{1}{2}MgSO_4$

(1) To find *c*. If *x* represents the distance *Qc* ÷ distance QR then $15 - (15 - 12.4)x =$ KCl per $1000H_2O$ at *c* and $48.6 + (100.2 - 48.6)x = \frac{1}{2}MgCl_2$ at c. Further, since only $MgSO_4.7H_2O$ and NaCl are separated between *a* and *c* the ratio KCl ÷ $\frac{1}{2}MgCl_2$ at *c* must equal the ratio of the original solution, namely 2 ÷ 14.6. Hence, $(15 - 2.6x) \div (48.6 + 51.6x) = 2 \div 14.6$ from which $x = 0.863$. The composition of *c* can then be calculated to be:

$1000H_2O$ — 18.8NaCl — 12.76KCl — 93.12 $\frac{1}{2}MgCl_2$ — 17 $\frac{1}{2}MgSO_4$

(2) To find *w*. If the crystallization path *bc* be followed in the direction of *b* it would intersect BQ at some point, which will be designated by *w*. If *y* represents the distance *Bw* ÷ BQ then $0 + (15 - 0)y =$ KCl per $1000H_2O$ at *w* and $53.8 - (53.8 - 48.6)y = \frac{1}{2}MgCl_2$ per $1000H_2O$ at *w*. Further, the ratio KCl ÷ $\frac{1}{2}MgCl_2$ in the solution which is being evaporated is the same at *w* as at *a* and hence $(0 + 15y) \div (53.8 - 5.2y) = 2 \div 14.6$ from which $y = 0.469$. The composition of *w* may then be calculated to be:

$1000H_2O$ — 46.22NaCl — 7.034KCl — 51.36 $\frac{1}{2}MgCl_2$ — 26.96 $\frac{1}{2}MgSO_4$

(3) To find *b*. If *z* represents the distance *wb* ÷ *wc* then $7.034 + (12.76 - 7.034)z =$ KCl per $1000H_2O$ and 26.96 —

$(26.96 - 17)z = \frac{1}{2}MgSO_4$ at b and since the ratio $KCl \div \frac{1}{2}MgSO_4$ in the solution being evaporated does not begin to change until b is reached $(7.034 + 5.73z) \div (26.96 - 9.96z) = 2 \div 7.2$, from which $z = .054$. The composition of b can then be calculated to be:

$$1000H_2O - 44.74NaCl - 7.34KCl - 53.6\ \tfrac{1}{2}MgCl_2 - 26.44\ \tfrac{1}{2}MgSO_4$$

(4) To calculate changes from a to R. Knowing the composition of b and c the amounts of H_2O, NaCl and $MgSO_4.7H_2O$ which separate when 1000 moles of water, associated with $94NaCl - 2KCl - 14.6\ \frac{1}{2}MgCl_2 - 7.2\ \frac{1}{2}MgSO_4$, are evaporated can be calculated as follows:

If $x =$ NaCl lost from a to b then $(94 - x) \div 2 = 44.74 \div 7.34$, from which $x = 81.8$ and NaCl left in solution $= 12.20$.

If $y = H_2O$ lost from a to b then $12.2 \div (1000 - y) = 44.74 \div 1000$, from which $y = 727.3$ and H_2O left in solution $= 272.70$.

If $x =$ NaCl lost from b to c then $(12.2 - x) \div 2 = 18.8 \div 12.76$, from which $x = 9.253$ and NaCl left in solution $= 2.947$.

If $y = H_2O$ lost from b to c then $(2.946) \div (272.7 - y) = 18.8 \div 1000$, from which $y = 116$ and H_2O left in solution $= 156.70$.

If $z = MgSO_4$ lost from b to c then $2 \div (7.2 - 2z) = 12.76 \div 17$, from which $z = 2.267$ and $\frac{1}{2}MgSO_4$ left $= 2.666$.

If $p = MgSO_4.7H_2O$ and $q =$ schönite lost from c to R then $(2 - 2q) \div (17.266 - 2p - 2q) = 12.4 \div 115$, and $(2 - 2q) \div (2.666 - 2p - 4q) = 12.4 \div 14.8$ from which $p = .07$ and $q = .086$ and there remains in solution 1.828 KCl, 16.954 $\frac{1}{2}$Mg and 2.182 $\frac{1}{2}SO_4$.

If $x =$ NaCl lost from c to R then $(2.946 - x) \div (2 - .172) = 14.8 \div 12.4$, from which $x = 0.768$ and NaCl left in solution $= 2.178$.

If $y = H_2O$ lost from c to R then $(2.946 - 0.768) \div (156.74 - y) = 14.8 \div 1000$, from which $y = 9.58$ and H_2O left in solution $= 147.12$.

(5) To calculate changes from R to S.

If $x = NaCl$, $y = H_2O$, $p = MgSO_4.7H_2O$ and $q = KCl$ which separate from R to S, then $(1.828 - q) \div (16.954 - 2p) = 9.2 \div 139$, and $(1.828 - q) \div (2.181 - 2p) = 9.2 \div 9$, from which $q = 0.783$ and $p = 0.579$; also
$(1.828 - q) \div (2.178 - x) = 9.2 \div 62$, from which $x = 1.473$; also
$(1.828 - q) \div (147.12 - y) = 9.2 \div 1000$, from which $y = 33.53$.
Hence the residual solution contains
$113.59H_2O$, $0.705NaCl$, $1.045KCl$, $15.796\ ½Mg$, $1.024\ ½SO_4$.

(6) To calculate changes from S to T.

If $x = NaCl$, $y = H_2O$, $p = MgSO_4.7H_2O$ and $q =$ carnallite, which separate from S to T, then $(1.045 - q) \div (15.796 - 2p - 2q) = 0.4 \div 208.8$, and $(1.045 - q) \div (1.024 - 2p) = 0.4 \div 12$, from which $q = 1.019$ and $p = 0.121$; also, $(1.045 - q) \div (0.705 - x) = 0.4 \div 1.4$, from which $x = 0.614$; also $(0.705 - x) \div (113.59 - y) = 1.4 \div 1000$, from which $y = 48.57$. Hence, the residue solution contains:
$65.02H_2O - .091NaCl - .026KCl - 13.516\ ½Mg - 0.782\ ½SO_4$.

The substances eliminated at each stage of the evaporation can be tabulated as follows:

a to *b*	$727.3H_2O$	$81.800NaCl$			
b to *c*	$116.0H_2O$	$9.253NaCl$	$2.267MgSO_4$		
c to R	$9.58H_2O$	$0.768NaCl$	$0.070MgSO_4$	0.086	schönite
R to S	$33.53H_2O$	$1.473NaCl$	$0.579MgSO_4$	0.783	sylvine
S to T	$48.57H_2O$	$0.614NaCl$	$0.121MgSO_4$	1.019	carnallite
Residual solution	$65.02H_2O$	$0.091NaCl$	$0.391MgSO_4$	0.026	carnallite $5.95MgCl_2$

In this table the water associated with the hydrated salts has been included in the first column; that eliminated as vapor or present in the residual solution would be less than the figures given.

Results of Evaporation of Sea Water at Various Temperatures. The series of changes which take place when sea water is evaporated at 25°, 55° and 83° can be followed by use of a similar

series of calculations. At 25° the first solid, in addition to NaCl, which separates is astracanite. The crystallization path then intersects the line separating the astracanite and epsomite fields, at which point the astracanite will be converted into epsomite, then crosses a small portion of the epsomite field, with further separation of epsomite, and finally reaches a three-solid crystallization path at which kainite begins to appear. Further evaporation yields successively epsomite and kainite, hexahydrate and kainite, kieserite and kainite, kieserite and carnallite, and yields a solution saturated as to kieserite, carnallite and bischofite at the crystallization end-point.

At 55° the first solid to separate in addition to halite is löweite. The crystallization path then intersects the line separating the löweite and langbeinite fields, at which the separated löweite is converted into langbeinite, crosses the langbeinite field till it intersects the line separating the langbeinite and kainite fields, at which the separated langbeinite is converted into kainite, crosses a small portion of the kainite field until it intersects the line separating the kainite and kieserite fields, at which point kainite is converted into kieserite and then crosses the kieserite field, reaching the three-solid crystallization path at which kieserite and carnallite are stable solids. Further evaporation yields carnallite and kieserite until the crystallization end-point is reached at which bischofite also appears.

At 83° the first solid in addition to halite to separate is löweite. The crystallization path then intersects the line separating the löweite and kieserite fields, at which point löweite is changed into kieserite, then crosses the kieserite field and meets the three-solid crystallization path at which carnallite also appears. Further evaporation yields carnallite and kieserite until the crystallization end-point is reached with bischofite as the additional solid.

Geological Significance of the Stassfurt Salt Investigations. Correlation of the facts relating to the paragenesis of the minerals which can be derived from the evaporation of sea water, with those derived from a study of the Stassfurt Deposits is of extreme interest from a geological point of view. The problem here suggested is a more complex one than the bare statement of it indicates. The unknown variables, which it is especially desirable to evaluate, are the composition of the solution from which these beds were derived, and the temperature at which they were laid

down. If the entire body of solution concerned in this formation had been evaporated at an approximately constant temperature in a basin of uniform depth, and if there were no subsequent alterations due to changes in temperature, to the introduction of further quantities of sea water or to the leaching action of ground waters, and no tectonic disturbances, the entire problem might be solved with ease and certainty. An examination of the beds clearly shows that none of these assumptions are justifiable.

Strata of the Stassfurt Deposits. The lowest strata of the various deposits collectively known as Stassfurt deposits are composed of alternate layers of anhydrite and halite, the whole attaining a thickness of some seven hundred meters as a maximum. The anhydrite layers vary from a few millimeters to several centimeters in thickness, forming a series of "annual rings" which clearly indicate periodic changes in the temperature which prevailed during their deposition. Presumably the anhydrite layers were formed during the warmer part of the seasonal cycle since the solubility of this mineral decreases with increasing temperature, and the halite layers during the colder portion of the cycle since its solubility decreases slightly with decreasing temperature. Above the anhydrite region that mineral is replaced in a similar manner by polyhalite but the total thickness of this region does not exceed sixty meters. Above this is the kieserite region, also some sixty meters thick, and above this the carnallite region which reaches a thickness of fifty meters. The boundaries of the four regions are in some deposits poorly defined or entirely unrecognizable. Halite is found throughout the entire geological column but the percentage found decreases from 95 per cent in the anhydrite region to 5 per cent in the carnallite region.

In addition to the deposits which surround the city of Stassfurt there are similar deposits of greater extent and richness as to potassium containing minerals at or near Hanover, a region south of the Hartz Mountains, Halle and at Werra in Thuringia. These localities are at the present time producing much larger amounts of potassium containing minerals than the original Stassfurt mines. The potassium and magnesium containing strata, which succeed the polyhalite beds, have been investigated by Rozsa.[2] He found in the deposits of Stassfurt, South-harz and Hanover two types of beds, namely (A), those composed of alternate layers of halite

[2] Rozsa, *Kali, 7,* 505 (1913).

and "hauptsalz," that is, mixtures of carnallite, kieserite and halite, and (B), those composed of alternate layers of halite and "hartsalz," that is a composite mixture of halite, sylvite and kieserite. Measurements of the thickness of the different layers which make up both the A and the B types of beds of the regions named show striking similarities as to their order and relative thickness, and clearly indicate that the same cycle of changes was concerned in their deposition. Furthermore, a remarkable correlation was found to exist between the A type and the B type of beds which is shown

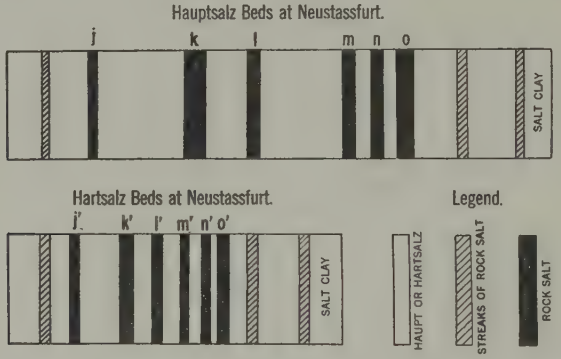

FIG. 77.—Diagrammatic representation of salt beds in strata at Neustassfurt.

in the accompanying diagram, Figure 77. The correlation between the different halite layers, which can be used as indicators, is made clear by the use of letters and the conclusion seems unescapable that beds of the B type were derived from those of the A type, chiefly by the elimination of magnesium chloride. Correlation of the hauptsalz and hartsalz strata was also established through the discovery of intergrading deposits although these correlations were in many cases greatly affected by local disturbances.

In deposits of the "Werratype," which includes beds from a large number of widely separated regions, a somewhat different correlation was established. These are illustrated by the accompanying sketch, Figure 78, which represents beds of the Alexandershall saltworks. It will be noted that the thick carnallite strata, which are interspersed with the layers of halite, have been partially transformed on both surfaces into sylvinite, which is an intimate mixture of halite and sylvite, and hartsalz, presumably by the

action of a solution saturated as to halite but unsaturated as to magnesium chloride or carnallite. The thick deposits labeled blue sylvanite, however, represent the result of a more complete and more complex series of changes in which the carnallite strata have been changed into coarse-grained sylvanite by the loss of both magnesium chloride and magnesium sulfate. At the Bleicherode works strata showing the successive changes kieserite-carnallite → kieserite-sylvinite → sylvinite-carnallite were observed. The last of these clearly represents a reformation of carnallite, which could only result from the action of a concentrated solution of magnesium chloride on potassium chloride.

These facts make it clear that the beds in question have under-

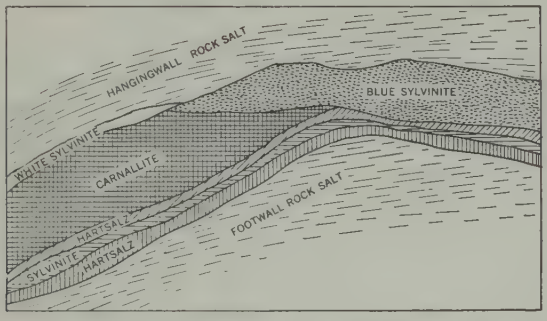

FIG. 78.—Strata of the salt beds at Alexandershall.

gone profound changes since they were first laid down. It is necessary to assume the presence of large concentrations of magnesium chloride to account for the presence of carnallite but deposits of bischofite, which must have separated in large amounts if the crystallization end-point was reached, are entirely lacking. This and much of the magnesium sulfate must have been eliminated after the primary deposition, and the uppermost strata now found must be mere fragments of those originally formed.

Average Chemical Composition of the Strata. Some insight into the nature of the changes may be gained by a study of the average chemical composition of the different layers. From data obtained by Reidel,[3] D'Ans calculated the average molal composition of a column of uniform diameter cut through the polyhalite,

[3] Reidel, *Zeit. Kryst, 50,* 139 (1913); D'Ans, *Kali, 9,* 268 (1915).

kieserite and carnallite strata of the Berlepsche mine of Stassfurt. His results showed the following facts:

1. The ratio of K to SO_4 for the entire column was 1 : 2.75; for sea water it is 1 : 3.6. Since this section should include all of the K and SO_4 of the original solution it is clear that a large part of the SO_4 must have been eliminated.

2. The ratio of the K to Mg was 1 : 4.33 and for sea water it is 1 : 10.09, also the ratio of SO_4 to Mg was 1 : 1.57 and for sea water it is 1 : 3. These facts clearly require the elimination of enormous amounts of Mg, for the most part as $MgCl_2$.

3. The calculated changes resulting from the evaporation of sea water at all four temperatures show that the largest part of the SO_4 should separate in the kieserite region but these analyses show more SO_4 in the carnallite than in the kieserite and polyhalite regions combined.

4. The amount of halite in all these regions is so much greater than that calculated for the evaporation of sea water that it is necessary to assume periodic additions of further quantities of halite-yielding solution.

Temperature at Which the Stassfurt Beds Were Formed. Another characteristic of the Stassfurt deposits generally is the very limited amount of kainite present. This mineral should be found in large quantities in the kieserite and carnallite zones provided the temperature at which the beds were formed did not exceed 83°. The beds in which it has been found show secondary action and it is doubtful whether it ever occurs as a primary product. Presumably the large amounts of kainite originally formed have been converted into hartsalz as represented by the reaction:

$$KCl.MgSO_4.3H_2O + NaCl \rightarrow KCl + MgSO_4.H_2O + NaCl + 2H_2O.$$

It has also been shown by Rozsa[4] by comparing the results of analyses of sections of the haupt- and hartsalz sections of the Berlepsche mine that hartsalz may be derived directly from carnallite in accordance with the equation:

$$xKMgCl_3.6H_2O + yMgSO_4.H_2O + zNaCl \rightarrow KCl + yMgSO_4.H_2O + xMgCl_2.6H_2O + zNaCl.$$

[4] Rozsa, *Z. anorg. Chem.*, *94*, 92 (1915).

Both of these processes require a minimum temperature of 72°. The presence of certain other minerals especially of langbeinite, löweite and vanthoffite whose formation requires temperatures of at least 37°, 43°, and 46° respectively, also make it necessary to assume that the primary beds have been heated to temperatures greatly in excess of those now prevailing at the surface of the earth. Indications of secondary heating have also been deduced from a study of the paragenetic relations observed in certain beds, but in view of the large amount of alteration to which the beds have been subjected such evidence is not conclusive.

The final conclusions of Rozsa [5] were that the original beds consisted of halite, kieserite and carnallite in varying proportions in different zones. Subsequent processes have resulted in the formation of sylvite from carnallite, vanthoffite and löweite from mixture of halite and kieserite and löweite, glaserite and langbeinite from halite, kieserite and carnallite.

[5] Rozsa, *Z. anorg. Chem.*, *86*, 163 and *91*, 318 (1915).

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